Docket No.: 00306-00355-US
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Gregory C. Volgas et al.

Application No.: 10/784,343 Confirmation No.: 2346

Filed: February 23, 2004 Art Unit: 1616

For: MANUFACTURE AND USE OF A HERBICIDE FORMULATION Examiner: A. N. Pryor

APPEAL BRIEF

MS Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Madam:

As required under § 41.37(a), this brief is filed within two months of the Notice of Appeal filed in this case on January 19, 2010, and is in furtherance of said Notice of Appeal.

This brief contains items under the following headings as required by 37 C.F.R. § 41.37 and M.P.E.P. § 1205.2:

I. REAL PARTY IN INTEREST

The real party in interest for this appeal is:

HELENA HOLDING COMPANY

II. RELATED APPEALS AND INTERFERENCES

There is a related appeal that was filed in U.S. Serial No. 09/916,611 (" '611 applicatiion"). However, the Board has not yet rendered a Decision in the '611 application. The '611 application is the parent application of this application. There are no interferences, or judicial proceedings which will directly affect or be directly affected by or have a bearing on the Board's decision in this appeal.

III. STATUS OF CLAIMS

A. Total Number of Claims in Application

There are 12 claims pending in application.

B. Current Status of Claims

1. Claims canceled: 1-90 and 92-93
2. Claims withdrawn from consideration but not canceled: 0
3. Claims pending: 91 and 94-104
4. Claims allowed: 0
5. Claims rejected: 91 and 94-104

C. Claims On Appeal

The claims on appeal are claims 91 and 94-104.

IV. STATUS OF AMENDMENTS

Applicant did not file an Amendment After Final Rejection.

V. SUMMARY OF CLAIMED SUBJECT MATTER

The claims on appeal are claims 91 and 94-104. These claims stand or fall together. Claims 91 and 104 are the only independent claims. Claim 91 states:

A microemulsion-forming-concentrate **consisting of** a herbicide compound in acid form and at least one surfactant, wherein the concentrate can be combined with water to form a microemulsion wherein the herbicide in the acid form is 2,4-dichlorophenoxyacetic acid or dicamba acid or a mixture thereof and wherein said surfactant consists of

Alcohol alkoxylate,

Alcohol alkoxylate sulfate,

Alkylphenol alkoxylate,

Alkanolamide,

Alkylaryl sulfonate,

Amine oxide,

Betaine,

Block polymers of ethylene and propylene oxide,

Carboxylated alcohol or alkylphenol alkoxylate,

Diphenyl sulfonate,

Ethoxylated amine,

Ethoxylated fatty acid,

Ethoxylated fatty ester and oil,

Ethylene carbonate,

Fatty ester,

Glycerol ester,

Phosphate ester surfactant,

Sarcosine,
Sorbitan,
Sucrose,
Glucose,
Sulfate of alkoxylated alkylphenol ,
sulfonate of alkoxylated alkylphenol,
Sulfate of alcohol or
Tristyrylphenol Alkoxylate. **Support for the term microemulsion can be found in examples 1, 2, 4 and 7 which are microemulsions and are very similar to the examples cited in U.S. Patent No. 6,803,345 ("Herold"), support for the herbicide in the acid form can be found in the specification at page 5, lines 1-5 and in examples 1, 2, 4 and 7; support for the surfactant can be found in the specification at page 6, line 8 through page 8, line 9.**

104. A microemulsion-forming-concentrate **consisting of** a herbicide compound in acid form and surfactant, wherein the concentrate can be combined with water to form a microemulsion and wherein the herbicide in the acid form is 2,4-dichlorophenoxyacetic acid and said surfactant of
Alcohol alkoxylate,
Alcohol alkoxylate sulfate,
Alkylphenol alkoxylate,
Alkanolamide,
Alkylaryl sulfonate,
Amine oxide,
Betaine,
Block polymers of ethylene and propylene oxide,

Carboxylated alcohol or alkylphenol alkoxylate,
Diphenyl sulfonate,
Ethoxylated amine,
Ethoxylated fatty acid,
Ethoxylated fatty ester and oil,
Ethylene carbonate,
Fatty ester,
Glycerol ester,
Phosphate ester surfactant,
Sarcosine,
Sorbitan,
Sucrose,
Glucose,
Sulfate of alkoxylated alkylphenol ,
sulfonate of alkoxylated alkylphenol,
Sulfate of alcohol or
Tristyrylphenol Alkoxylate.

Support for the term microemulsion can be found in examples 1, 2, 4 and 7 which are microemulsions and are very similar to the examples cited in U.S. Patent No. 6,803,345 ("Herold"), support for the herbicide in the acid form can be found in the specification at page 5, lines 1-5 and in examples 1, 2, 4 and 7; support for the surfactant can be found in the specification at page 6, line 8 through page 8, line 9.

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

1. Claims 91 and 94-104 were rejected under 35 U.S.C. 103(a) as being obvious over US 5,558,806 ("Policello").

VII. ARGUMENT

A. Group I (Claims 91 and 94-104)

1. Claims 91 and 94-104 were rejected as being obvious over Policello.

This application was filed to provoke an interference with Herold et. al., U.S. Patent No. 6,803,345 ("Herold"). The Examiner has acknowledged this in several of the Office Actions including the last Final Office Action mailed September 18. 2009, in the middle of page 8, of under the heading "Other Matters.

Claim 1 of Herold states:

1. A microemulsion-forming-concentrate comprising herbicide compound in acid form and surfactant, wherein the concentrate can be combined with water to form a microemulsion.

Herold, was published on August 7, 2003 and claims benefit to an earlier filing date of September 26, 2001. The original Claim 104 was identical to claim 1 of Herold. Claim 104 has subsequently been narrowed during the prosecution of this application. Claim 91 corresponds to claims 1-3 of Herold. Since claim 92 uses closed language "consisting of" and excludes any other ingredients, claim 92 encompasses claims 4 and 5 of Herold. Claim 93 corresponds to claim 6 of Herold. Claim 94 corresponds to claim 7 of Herold. Claim 95 corresponds to claim 8 of Herold. Claim 96 corresponds to claims 9-11 of Herold. Claim 97 corresponds to claim 12 of Herold. Claim 98 corresponds to claim 13 of Herold. Claim 99-103 corresponds to claims 21, 29, 30, 31, 32 and 33 of

Herold. Examples 1, 2, 4 and 7 were disclosed in the provisional application Serial No. 60/250,547 filed December 1, 2000. This is over 9 months before the provisional application of Herold was filed.

The applicant respectfully requested that an interference be declared. The applicant proposed that the count of the interference should be

(a) claim 1 of Herold or

(b) claim 1 of Herold or claim 91 of this application.

The applicant believes the claims 91-103 of this application would correspond to count 1. The applicant believes that all the allowed claims of Herold, claims 1-13, 21-23 and 29-36 would correspond to count 1. None of the Herold's claims are patentably distinct.

The applicant copied the claims and provided support in the second preliminary amendment filed June 10, 2004.

The applicant's independent claims 91 and 104 claim a microemulsion-forming-concentrate comprising herbicide compound (2,4-dichlorophenoxyacetic acid and/or dicamba) in acid form and surfactant (specific ones being claimed), wherein the concentrate can be combined with water to form a microemulsion.

The invention is drawn to a method for manufacture and use of a herbicidal formulation of chlorinated carboxylic acid herbicides **in the acid form**. As disclosed in the applicant's background of the invention,

> [m]any agricultural formulations contain **water-soluble salts of chlorinated carboxylic acid herbicides**. These salts, often alkylamine salts or metal salts, **are generally not as active as their acid equivalents**. For

> example, (2,4-dichlorophenoxy)acetic acid ("2,4-D") acid is known to be more herbicidally active than the dimethylamine salt of 2,4-D.
>
> . . .
>
> **Another problem associated with the amine salts of some chlorinated carboxylic acid herbicides is their inability to mix with fertilizers**. 2,4-D amine herbicides cannot be mixed directly into Uran (urea-ammonia nitrate) fertilizer **without some dilution in water**. This is a disadvantage for applicators, since this dilution practice increase the total spray volume they must apply per acre. (emphasis added) (see pages 1-3 of the specification).

As stated above, it was recognized that the prior art uses chlorinated carboxylic acid herbicides in the salt form. The applicant has found a way to use the more active chlorinated carboxylic acid herbicides in the acid form preferably by dissolving the acid herbicide in a surfactant. These formulations have shown superior herbicidal activity when compared to standard salt and ester forms (see the abstract).

The key features of the applicant's claimed invention are

1. A microemulsion-forming concentrate **CONSISTING OF** a herbicide compound in the acid from and at least one surfactant. **The claim uses closed language "consisting of".**

2. A microemulsion which is made by blending the herbicide compound in the acid form with at least one surfactant.

3. A chlorinated carboxylic acid herbicide (2,4-dicholorphenoxy acetic acid and/or dicamba in the acid form.

The first time the claims were rejected over Policello was January 31, 2008. None of these features are present in Policello. Policello would not lead a person of ordinary skill in the art to even investigate the solubility of the herbicide in the surfactant (regardless of the form of the herbicide). Policello does not lead one of ordinary skill in the art to investigate the use of the acid form of the phenoxy herbicides. Below is a table referring to the sections cited by the Examiner at page 3 of the Office Action mailed January 31, 2008, for Policello along with the applicant's comment about the particular section.

Abstract	The abstract discloses the use of a surfactant blend and it's use as an adjuvant for pesticide formulations. The abstract provides no disclosure of phenoxy herbicides in any form. Nor does the abstract provide any indication of the claimed microemlsion. The surfactant blend requires a specific silicone surfactant (which is explicitly excluded from the applicant's claimed invention with the use of "**consisting of**" language and a second surfactant).
Col. 2, line 21 - col. 4, line 27	This section more fully describes the surfactant blend of the invention. The surfactants include a specific silicone surfactant (which is explicitly excluded from the applicant's claimed invention with the use of "**consisting of**" language and a second surfactant). The second surfactant is either an alcohol alkoxylate surfactant or an alkyl polyglucoside surfactant. This section provides no disclosure of phenoxy herbicides in any form. This section requires a specific silicone surfactant which is excluded from the applicant's claimed invention. Nor does this

	section provide any indication or a microemulsion.
Col. 6, lines 26-42	This section discloses the pesticides for which the invention is useful. The section discloses 2,4-D and dicamba along with several other growth regulators (see col. 6, line 26- col. 8, line52). **Note that the usefulness of the surfactant blend is determined by the spreading of the foliarly applied pesticide spray (see Column 6, lines 18 – 24.** The surfactant blend is simply used as a spreader for foliar sprays of the listed pesticides.
Col. 9, line 52 - col. 10, line 2	This section simply describes additional and optional components of the invention.
Example 4	This example provides no disclosure of phenoxy herbicides in any form. The surfactant blend in example 4 requires a silicone surfactant which is excluded from the applicant's claimed invention because of the "consisting of" language.

Policello at Col. 9, lines 19-23 and 32-36 describes the inclusion of the claimed surfactant blend into general pesticide formulations and their further dilution with water. This section provides no disclosure of phenoxy herbicides in any form.

A detailed discussion of the examples is as follows: Examples 1 – 4 discloses the spreading characteristics of the surfactant blends which require a specific silicon surfactant which is excluded from the applicant's claimed invention. These solutions do not contain any pesticide or herbicide. It appears that Example 2 is missing or is described at col. 13, lines 29-34.

Example 5 Employs the surfactant blend (which requires a specific silicon surfactant which is **excluded** from the applicant's claimed invention) used as an additive for the separate pesticide formulation known as Reflex®. The label for the product Reflex shows clearly that the active ingredient *fomasafen* is in the **sodium salt form** (see Appendix B). However, referencing back to the large laundry list of pesticides which the inventor claims, (See Column 8, lines 38 – 41), fomasafen is listed simply as fomasafen. In this laundry list, the inventor clearly did not see the need to describe esters and salts of the actives because those would be obvious to one skilled in the art.

Example 6 discloses compositions containing the claimed silicone surfactant blend (which require a specific silicon surfactant which is excluded from the applicant's claimed invention) and a mineral oil. Again, the purpose of the surfactant blend is to provide spreading. These compositions do not contain any pesticide or herbicide.

Clearly as stated above, Policello does not disclose the applicant's three required features.

1. The applicant's claimed invention requires consisting of language!

Policello requires the use of surfactant blend with requires polyalkylenoxide polysiloxane and a short chain hydrophobic moiety. Again, the applicant excludes the use of polyalkylenoxide polysiloxane surfactants by using "CONSISTING OF" language. For this reason alone this rejection must be withdrawn!

2. A microemulsion which is made by blending the herbicide compound in the acid form with at least one surfactant

Policello at col. 2, lines 2-11, defines the intended scope of the invention as:

"....provides for the acceptable **dispersion**, of pesticide actives without significantly interfering with the spreading capability....."

and

"....can more effectively **emulsify** water-insoluble agricultural products."

(emphasis added)

Policello teaches away from the applicant's claimed invention because Policello is trying to emulsify the water-insoluble (salt) agricultural products while the applicant is fully dissolving the acid herbicide in the acid form and not the salt form in the surfactant. For this reason alone, the applicant believes Policello is not appropriate prior art and teaches away from the applicant's claimed invention. There is no disclosure or teaching of the solubilizing of pesticide actives.

3. A chlorinated carboxylic acid herbicide (2,4-dicholorphenoxy acetic acid and/or dicamba in the acid form.

Furthermore, the Examiner is focusing on prior art that taught the use of 2,4-D acid in combination with a surfactant. The applicant does not believe that Policello teaches anything about 2,4-D in the **acid form**.

Assuming arguendo, that Policello teaches ANYTHING about 2,4-D acid, there is still no motivation to omit a solvent. Further enclosed in Appendix B is a copy of a Declaration executed may 13, 2008 by Johnnie Roberts that was submitted in the parent application that established that silicone surfactants according to Policello are unstable in the inherent acidic conditions according to the applicant's claimed invention (see attached declaration in Appendix B). As stated in paragraph no. 24 of the declaration. "... the acid herbicide would not be able to

fully dissolve in the silicone surfactant according to Policello, without significant degradation of the silicon surfactant."

The following two examples of prior art that Examiner has previously considered:

1. AF-300 This formulation was what one of ordinary skill in the art would do if his intention was to formulate a combination of 2,4-D acid and a surfactant. As demonstrated in Johnnie Robert's declaration executed August 29, 2005, the formulation experts at Nufarm had to employ a conventional solvent (petroleum distillates) to dissolve the 2,4-D acid. They did not test higher and higher levels of surfactant to try and dissolve the 2,4-D acid because to one of ordinary skill in the art, that would make no sense.
2. Weedone 638 This formulation was disclosed in the applicant's specification at page 2, lines 13-20. In this formulation, the surfactant again is not sufficient to dissolve the 2,4-D acid. The 2,4-D ester and the petroleum distillates are used to dissolve the 2,4-D acid. Again, the formulation experts at the time did not try to raise the surfactant levels in this formulation to dissolve the 2,4-D acid. To one of ordinary skill in the art, that would have made no sense. It made more sense to increase the amount of petroleum distillates.

The Examiner has stated that it would have been a simple matter of testing for a formulation chemist to determine what level of surfactant was required to dissolve the acid herbicide. This is true, but only in hindsight. No formulation chemist of ordinary skill in the art would have tried to dissolve the herbicide in anything but more solvent, like petroleum distillates.

To describe the ordinary skill in agricultural formulations, one can find numerous references. In 1997, a multi-industry, international forum was held to discuss formulation chemistry across several industries. Dr. Kozo Tsuji of Sumitomo provided an overview of the state of the art in pesticide formulations. The proceedings from this forum are bound in a book entitled **Formulation Science.**

Dr. Tsuji's chapter discloses the following details on pesticide formulations:

Page 57 cites potential improvements in EC's as:

"Use water, convert to solid formulations or change the solvents or the emulsifiers."

Nowhere does the **Formulation Science** of the day indicate that the emulsifiers (a.k.a surfactants) might actually be one and the same as the solvent.

Page 60 shows a typical **emulsifiable in water formulation (EW):**

Line 14 "Solid pesticides are dissolved at first in water-insoluble organic solvents, and then dispersed in water."

Page 61 describes a **suspension concentrate (SC).** In these formulations, the pesticide is suspended and not dissolved.

Page 62 describes a **Suspoemulsion (SE).** In these formulations, one active ingredient is formulated with traditional organic solvents in the same manner as an **EW**. This emulsifiable concentrate is then suspended in another water based suspension that has been formulated in the same manner as an **SC.**

Page 63 describes a **Microemulsion (ME).** As with **EW** formulations, solid active ingredients are first dissolved in organic water immiscible solvents. Emulsifiers (surfactants) are then added to produce an emulsion.

Page 63-64 describes a **Multiple Emulsion.** This formulation type is produced in much the same manner as **EW** formulations but said **EW** is further emulsifier in water to reduce formulation toxicity.

Other formulations described in page 64-65 of this review are solid formulations and thus irrelevant.

Another reference to establish the "ordinary skill in the art" is found in Purdue University's publication **Pesticides and Formulation Technology** (Purdue Pesticides Programs). This publication discusses on page 15 the normal formulation process for active ingredients. Specifically, an appropriate solvent is selected, and only then are appropriate emulsifers (surfactants) selected.

Yet another reference is used to establish the "ordinary skill in the art" is found in Rhodia's **Auxiliaries for agrochemical formulations.** In section 3-2, emulsifiable concentrate formulations are described. In short, for a liquid pesticide formulation that will mix with water, you normally have three components:

- The active ingredient
- A solvent

- Emulsifiers (surfactants)

The Examiner has a burden to demonstrate the motivation for one of ordinary skill in the art to increase the surfactant to the point where the acid herbicide fully dissolves.

- The only similar acid herbicide formulations available employed the use of traditional solvents to dissolve the active.
- No other formulations have been shown that use surfactants to fully solubolize **ANY** active ingredients.
- Descriptions of typical formulations in the field always employ a solvent of some kind that is separate from optional surfactants.
- The examiner has not provided one instance of a combination of ANY herbicide and ANY surfactant wherein the herbicide was fully solubolized in the surfactant, or further which excluded a traditional solvent (i.e. water, petroleum distillate).

Comments to the Examiner's Statements

At page 3, lines 9-10, of the final Office Action mailed December 18, 2009, the Examiner states, "[a] reference does not have to provide all possible scenarios to suggest an invention." However, the Examiner must still take into account the reference as a whole. "[R]ejections on obviousness cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness." *KSR International Co. v. Teleflex Inc.*, 82 USPQ2d 1385, 1396 (2007) quoting *In re Kahn*, 441 F.3d 977, 988 (Fed. Cir. 2006). Furthermore, the examiner cannot selectively pick and choose from the disclosed parameters without proper motivation as to a particular selection. The mere fact that a reference may be modified to reflect features of the claimed invention does not make the modification, and hence the claimed invention, obvious unless the prior art

suggested the desirability of such modification. *In re Mills*, 916 F.2d 680, 682, 16 USPQ2d 1430 (Fed. Cir. 1990); *In re Fritch*, 23 USPQ2d 1780 (Fed. Cir. 1992). Thus, it is impermissible to simply engage in a hindsight reconstruction of the claimed invention where the reference itself provides no teaching as to why the applicant's combination would have been obvious. *In re Gorman*, 933 F.2d 982, 987, 18 USPQ2d 1885, 1888 (Fed. Cir. 1991).

Applying the Examiner's logic, no further patents should be granted on ANY herbicide, because Policello suggests that herbicides might be useful. There MUST be some teaching of the art to suggest its use. As stated above, merely mentioning two words in the same patent does not teach anything about those two things.

At the bottom of page 3, of the final Office Action, the Examiner stated that Policello teaches that other surfactants can be added to the composition. Nowhere does Policello TEACH a composition **without** his silicone surfactant, and in fact, teaches away from such compositions. The silicone surfactant is what his patent is all about (see the title, abstract, summary of the invention, detailed description of the invention, the examples and the claims). Again, the applicant's claimed invention is

> a microemulsion-forming-concentrate **consisting of** a herbicide compound in acid form and at least one surfactant, wherein the concentrate can be combined with water to form a microemulsion wherein the herbicide in the acid form is 2,4-dichlorophenoxyacetic acid or dicamba acid or a mixture thereof and wherein said **surfactant consists of** . . . (emphasis added)

The silicone surfactant required by Policello is not included in the applicant's list of surfactants. The applicant uses "consists of" language (closed language) which would exclude the use of the silicone surfactant required by Policello.

At the top of page 5 of the final Office Action, the Examiner acknowledges that the applicant claims use "consisting of" language. However, the Examiner than states in the middle of page 5,

> While the "consist of" language excludes in the claim excludes Policello's silicon based surfactants, the Examiner still maintains that Policello's invention makes obvious instant combinations consisting of acid herbicide plus instantly named alcohol alkoxylate surfactants.

Again, nowhere does Policello TEACH a composition without his silicone surfactant, and in fact, teaches away from such compositions. The silicone surfactant is what his patent is all about (see the title, abstract, summary of the invention, detailed description of the invention, the examples and the claims). In addition, as stated above, it is impermissible to simply engage in a hindsight reconstruction of the claimed invention where the reference itself provides no teaching as to why the applicant's combination would have been obvious.

At page 5, line 8 of the final Office Action, the Examiner states that Policello's abstract discloses "composition does not require solvents". The abstract states, "[a] surfactant blend comprising a polyalkyleneoxide polysiloxane and an organic compound [surfactant]....as an adjuvant in pesticide sprays."

The Examiner incorrectly assumes that "pesticide sprays" could include 2,4-D acid. 2,4-D acid is a solid and could not be sprayed without something to convert it to a liquid. This is implied in Policello's term, "pesticide sprays". By using this term, and not simply "pesticide", Policello acknowledges that the pesticide is already in a sprayable form, i.e. liquid, i.e. uses a

solvent. The abstract makes the applicant's point even more clear that the surfactant blend of Policello was never contemplated as a solvent for the pesticide.

Again, at page 5, line 8 of the final Office Action, the Examiner stated that Policello at column 2, line 65- col. 6, line 24 discloses "composition does not require solvents". Policello discloses his unique surfactant blend and its use to provide a "dispersion of pesticide actives".

This makes the applicant's point again. A dispersion is not the same as a solution. At col. 6, lines 18-20, Policello discloses that his unique surfactant blend can be used to "improve the spreading of foliar applied pesticidal sprays". Policello includes 2, 4-D acid as one of the pesticidal sprays that can be improved.

Again, Policello uses the term "pesticidal sprays" which implies that the pesticide was already in a sprayable form, i.e. liquid. The surfactant has nothing to do with making the pesticide sprayable. It is being used in this sense merely to spread the "pesticidal spray" on a leaf surface.

A page 7, line 2 of the final Office Action, the Examiner refers to Policello, at column 9, lines 19-23 and 32-36 and states that Policello discloses a range of the surfactant and pesticide that fall within the applicant's claimed range.

The Examiner's attention is directed towards Policello column 9, lines 24 – 30. Policello further describes the use ranges of the pesticide in terms of a "final application solution". This "final application solution" is further described in column 9, lines 37 – 40. This is before he ever discusses the addition of the surfactant, implying that the surfactant has nothing to do with the sprayability of the pesticide active.

A page 8, lines 6-8 of the final Office Action, the Examiner states Policello teaches combinations of acid herbicides to surfactants. Using this logic, no further patents should be granted on ANY herbicide, because Policello suggests that herbicides might be useful. There MUST be some teaching of the art to suggest its use. Merely mentioning two words in the same patent does not teach anything about those two things.

VIII. CLAIMS

A copy of the claims involved in the present appeal is attached hereto as Appendix A. As indicated above, the claims in Appendix A include the amendments filed by Applicant on May 26, 2009.

Applicant believes no additional fee is due with this response. However, if a fee is due, please charge our Deposit Account No. 03-2775, under Order No. 00306-00355-US from which the undersigned is authorized to draw.

Dated: March 18, 2010

Respectfully submitted,

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APPENDIX A

Claims Involved in the Appeal of Application Serial No. 10/784,343

1-90. (Cancelled)

91. (Previously presented) A microemulsion-forming-concentrate consisting of a herbicide compound in acid form and at least one surfactant, wherein the concentrate can be combined with water to form a microemulsion wherein the herbicide in the acid form is 2,4-dichlorophenoxyacetic acid or dicamba acid or a mixture thereof and wherein said surfactant consists of

Alcohol alkoxylate,

Alcohol alkoxylate sulfate,

Alkylphenol alkoxylate,

Alkanolamide,

Alkylaryl sulfonate,

Amine oxide,

Betaine,

Block polymers of ethylene and propylene oxide,

Carboxylated alcohol or alkylphenol alkoxylate,

Diphenyl sulfonate,

Ethoxylated amine,

Ethoxylated fatty acid,

Ethoxylated fatty ester and oil,

Ethylene carbonate,

Fatty ester,

Glycerol ester,

Phosphate ester surfactant,

Sarcosine,

Sorbitan,

Sucrose,

Glucose,

Sulfate of alkoxylated alkylphenol ,

sulfonate of alkoxylated alkylphenol,

Sulfate of alcohol or

Tristyrylphenol Alkoxylate.

92- 93 canceled

94. (Previously Presented) The concentrate of claim 91 consisting of from 15 to 20 parts by weight of said herbicide compound in acid form, and from 80 to 85 parts by weight of said surfactant.

95. (Previously Presented) The concentrate of claim 91 consisting of 20 parts by weight of said herbicide compound in acid form, and 80 parts by weight of said surfactant.

96. (Previously presented) A microemulsion-forming-concentrate consisting of a herbicide compound in acid form and at least one surfactant, wherein the concentrate can be combined with water to form a microemulsion wherein the herbicide in the acid form is 2,4-dichlorophenoxyacetic acid or dicamba acid or a mixture thereof and wherein said surfactant is selected from the group consisting of C_{11} alcohol (3EO) ethoxylate, nonylphenol (6EO)

ethoxylate, polyoxyethylene (20) sorbitan monolaurate, C_{11} alcohol (6EO) ethoxylate phosphate ester and mixtures thereof.

97. (Previously presented) The concentrate of claim 91 consisting of: 80 parts by weight surfactant, 20 parts by weight herbicide compound in acid form selected from the group consisting of 2,4-dichlorophenoxyacetic acid, dicamba acid and mixtures thereof.

98. (Previously presented) A microemulsion-forming-concentrate consisting of a herbicide compound in acid form and at least one surfactant, wherein the concentrate can be combined with water to form a microemulsion wherein the herbicide in the acid form is 2,4-dichlorophenoxyacetic acid or dicamba acid or a mixture thereof and wherein the concentrate consists of from about 25 to about 30 parts by weight 2,4-dichlorophenoxyacetic acid, and from about 70 to about 75 parts by weight of said surfactant selected from the group consisting of a C_{11} alcohol (3EO) ethoxylate, C_{11} alcohol (6EO) ethoxylate phosphate ester and mixtures thereof.

99. (Previously presented) A microemulsion comprising the microemulsion-forming-concentrate as claimed in claim 91 and water.

100. (Previously presented) A method of applying a herbicide, the method comprising: preparing the microemulsion-forming-concentrate as claimed in claim 91, diluting the microemulsion concentrate with water to form a microemulsion and then applying the microemulsion to a plant.

101. (Previously presented) The method of claim 100, further comprising applying the herbicide composition to a plant to control plant growth, while the herbicide compound is in acid form.

102. (Previously presented) A method of preparing the microemulsion-forming-concentrate as claimed in claim 91, the method comprising combining said herbicide compound in acid form with said surfactant, to produce a microemulsion-forming-concentrate that can be combined with water to form a microemulsion.

103. (Previously presented) A method of preparing a microemulsion, the method comprising: preparing the microemulsion-forming-concentrate as claimed in claim 91, by a method comprising combining said herbicide compound in acid form with said surfactant to produce a microemulsion-forming-concentrate that can be combined with water to form a microemulsion, and combining the microemulsion-forming-concentrate with water to form a microemulsion.

104. (Previously presented) A microemulsion-forming-concentrate consisting of a herbicide compound in acid form and surfactant, wherein the concentrate can be combined with water to form a microemulsion and wherein the herbicide in the acid form is 2,4-dichlorophenoxyacetic acid and said surfactant of
Alcohol alkoxylate,
Alcohol alkoxylate sulfate,
Alkylphenol alkoxylate,
Alkanolamide,
Alkylaryl sulfonate,
Amine oxide,
Betaine,
Block polymers of ethylene and propylene oxide,
Carboxylated alcohol or alkylphenol alkoxylate,
Diphenyl sulfonate,
Ethoxylated amine,
Ethoxylated fatty acid,
Ethoxylated fatty ester and oil,
Ethylene carbonate,
Fatty ester,

Glycerol ester,
Phosphate ester surfactant,
Sarcosine,
Sorbitan,
Sucrose,
Glucose,
Sulfate of alkoxylated alkylphenol ,
sulfonate of alkoxylated alkylphenol,
Sulfate of alcohol or
Tristyrylphenol Alkoxylate.

APPENDIX B

1. Reflex label
2. Declaration executed May 13, 2008 by Johnnie Roberts
3. **Formulation Science** 1997
4. **Pesticides and Formulation Technology**
5. Auxiliaries for agrochemical formulations
6. Declaration executed August 29, 2005 by Johnnie Roberts

APPENDIX C

There are no related proceedings referenced in II. above, hence copies of decisions in related proceedings are not provided.

Docket No.: 00306-00142-USU
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Johnnie R. Roberts et al.

Application No.: 09/916,611 Confirmation No.: 2968

Filed: July 27, 2001 Art Unit: 1616

For: MANUFACTURE AND USE OF A HERBICIDE FORMULATION Examiner: A. N. Pryor

1.132 DECLARATION

MS AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450
Dear Sir:

1. I, Johnnie Roberts am a citizen of the United States of America and hereby declare and say as follows:

2. I am one of the inventors of the above referenced application. I am employed by Helena Chemical Company as a Manager of the Product Development Laboratory in Memphis, Tennessee. A copy of my most recent Curriculum Vitae is attached as Appendix A. In view of the above qualifications, I consider myself an expert in the field of agricultural compositions.
3. I have read and reviewed U.S. application Serial No. 09/916,611 (" '611 application") including the examples.
4. I have read U.S. Patent No. 5,558,806 issued to Policello ("Policello"),
5. I have had the following experiments conducted under my supervision.
6. I have had Examples 1-3 of the specification remade to determine the pH value of the examples:

7. Example 1:
15% 2,4-D acid,
85% C11 alcohol (3EO) ethoxylate.

8. Example 1 has a pH of 2.7 when mixed with deionized water at 1.0% v/v.

9. Example 2:
10% dicamba acid
85% Nonylphenol (6EO) ethoxylate

10. Example 2 has a pH of 2.4 when mixed with deionized water at 1.0% v/v.

11. Example 3:
10% MCPA acid
90% Pluronic L31

12. Example 3 has a pH of 2.6 when mixed with deionized water at 1.0% v/v.

13. In the '611 compositions, the polyalkyleneoxide polysiloxane surfactants disclosed by Policello would not be stable at a low pH.

14. Further evidence is shown in the article scanned from ASTM Publication STP 1234 (see Appendix B). In this article by Policello et.al., the inventor himself acknowledges the pH sensitivity of previously known polyalkyleneoxide polysiloxane surfactants.

15. None of the examples from the Policello patent contained any amount of any herbicide.

16. The Policello patent is centered on synergistic combinations of non-silicone surfactants combined with silicone surfactants. Policello measures such synergy by determining the spread diameter on transparencies (polyester film). However, the silicone surfactant is unstable in the acidic conditions required by formulating chlorinated carboxylic acid

herbicides in the acidic form. For these reasons, the exemplary art that I elected to use for the testing was:

17. **Silicone containing example 4**

Ingredients	% by weight
2,4-D acid (in the acid form)	20.0%
Silwet L-77	80.0%

18. Silwet L-77 is identified as Silicone 1 in Column 10 of the Policello patent.

19. I believe that Policello probably intended his surfactant compositions to be combined with the normal formulations of the herbicides available at the time of his application. Policello lists Fomasafen in column 8, line 38, but his Example 5, in which Policello uses his claimed invention as an adjuvant with REFLEX®, which is actually the sodium salt of Fomasafen. At the time of Policello's invention, the commercial forms of 2,4-D were either amine salts or ester formulations. Because the amine salt form is water soluble, I selected the following comparative example:

20. **Silicone containing example 5**

Ingredients	% by weight
Dimethylamine salt of 2,4-D	20.0%
Silwet L-77	80.0%

21. I had prepared these formulations and then let the samples stand a room temperature for 4 days. After 4 days, the following solutions were prepared:

Solution A 0.10% of Silicone containing example 4 in 99.9% water

Solution B 0.10% of Silicone containing example 5 in 99.9% water

Solution C 0.08% of Silwet L-77 in 99.92% water (Chosen to provide equivalent amounts of the pure silicone surfactant as the formulated examples used in solutions A and B)

22. I then measured the spread diameters of 10 microliter droplets after 30 seconds (Policello column 11, line 34), on polyester film. The results are shown below:

Solution ID	Spread diameter of a 10 microliter droplet
Solution A	26 mm
Solution B	40 mm
Solution C	40 mm

23. The loss of spread ability as compared with the pure silicone surfactant (Solution C) even after only 4 days is evident in Solution A, which contains the Policello silicone surfactant and 2,4-D in the acid form. Solution B, which contains the dimethylamine salt form of 2,4-D and Policello's silicone surfactant does not show any loss of spreading ability.

24. Therefore the acid herbicide would not be able to fully dissolve in the silicone surfactant according to Policello, without significant degradation of the silicone surfactant.

25. I believe that this clearly demonstrates that the silicone surfactants of the Policello patent are unsuitable for use as the solubolizing surfactant of '611 invention.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18

of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

5-13-08

Johnnie Roberts Date

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Johnnie R. Roberts et al.

Application No.: 09/916611 Confirmation No.: 8709

Filed: August 29, 2005 Art Unit: 1616

For: MANUFACTURE AND USE OF A HERBICIDE FORMULATION Examiner: A. N. Pryor

37 CFR 1.132 DECLARATION

1. I am one of the inventors of the above referenced application. I am employed by Helena Chemical Company as a Director of Product Development and Technical Services in Memphis, Tennessee. A copy of my most recent Curriculum Vitae is attached as Appendix A. In view of the above qualifications, I consider myself an expert in the field of agricultural compositions.

2. I have reviewed the office action which was mailed on November 30, 2004. The examiner has rejected the claims based on composition of AF-300. I have also reviewed and am familiar with AF-300 along with the above identified application.

3. The composition of AF-300 is found on their Material Safety Data Sheet ("MSDS"). MSDS sheet, dated January 2002 (see Appendix 1).

This MSDS sheet shows the following composition:

2,4-Dichlorophenoxy acetic acid at 300 grams per liter
Synthetic ethoxylated alcohol at 50%
Solvent 400 at 235 grams per liter.

4. The formula from our Example 1 of the patent application was reproduced. It contained 85% of a C11 alcohol with 3 moles of ethylene oxide, and 15% 2,4-D acid. After the addition of the 2,4-D acid to the ethoxylated alcohol, the formulation became cloudy with chunks of 2,4-D technical dispersed. After 30 minutes of stirring at ambient temperature, the formulation was clear and the 2,4-D acid was fully solubolized. The odor exhibited with this formula, is very mild, and surfactant-like. This is very uncharacteristic of other commercial 2,4-D products. The odor can be a serious problem for applications of 2,4-D in sensitive areas, where neighbors may rightly fear herbicide drift. The flash point of the formula in Example 1 was over 200 degrees F. This places Example 1 in the non-flammable category with regards to shipping and storage.

5. As in the AF-300 disclosed formula, 235 grams per liter of kerosene was added to our Example 1. The solution immediately took on the odor of kerosene. Kerosene has an objectionable odor to most people, and may indicate to many neighbors that a herbicide application has been made nearby. Their real concern is really with herbicide drift, and when chemicals odors are detected, neighbors may be rightly concerned about injury to non-target plants.

6. The flash point of the kerosene containing formulation was 128 degrees F. This would require that shipments of this formula made by air would be classified as combustible. (See attached citation from 49 CFR 173 as Appendix B. Shipments made by ground would be considered combustible. Many states have strict requirements for storage of both combustible and flammable products. This could require consumers who store this product to make expensive modifications of their storage and containment areas.

7. Photos of the formulations are provided in an attached Powerpoint presentation.

8. I hereby declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

08-29-05
Date

Johnnie R. Roberts

Curriculum Vitae

Johnnie Roberts

July 22, 2005

Current job title with Helena Chemical Company: Director of Product Development and Technical Services

Education: Bachelor of Arts Degree with a Major in Chemistry – University of Tennessee – Martin

Job experience: 30 years experience in the formulation and development of Pesticide and Spray Adjuvant Products

Professional certification: Certified Crop Consultant: (CCA) 2000 – 20005

Publications: Co-Author of 10 Scientific papers dealing with the formulation and/or application of pesticides and spray adjuvants

Inventor of Record for the following patents:

PAT. NO.	Title
6,831,038	Agricultural formulation
6,541,424	Manufacture and use of a herbicide formulation
RE37,313	Homogeneous, essentially nonaqueous adjuvant compositions with buffering capability
6,232,272	Manufacture and use of herbicide chlorinated phenoxy formulation
5,906,961	Alkanolamide spreader-sticker surfactant combination
5,877,112	Agricultural formulation
5,741,502	Homogeneous, essentially nonaqueous adjuvant compositions with buffering capability
5,725,630	Dry granular fertilizer blend and a method of fertilizing plants
5,580,567	Homogeneous, essentially nonaqueous adjuvant compositions with buffering capability
5,393,791	Homogeneous, essentially nonaqueous adjuvant compositions with buffering capability
5,234,919	Water soluble, highly active dimethoate formulations in an alcohol/ester solvent system
5,178,795	Homogeneous, essentially nonaqueous adjuvant compositions with buffering capability

APPENDIX B

Citation from 49 CFR 173
Published 2004
Access via WWW at
http://www.access.gpo.gov/nara/cfr/cfr-table-search.html#page1

Sec. 173.120 Class 3--Definitions.

(a) **Flammable** liquid. For the purpose of this subchapter, a **flammable** liquid (Class 3) means a liquid having a flash point of not more than 60.5 [deg]C (141 [deg]F), or any material in a liquid phase with a flash point at or above 37.8 [deg]C (100 [deg]F) that is intentionally heated and offered for transportation or transported at or above its flash point in a bulk packaging, with the following exceptions:

(1) Any liquid meeting one of the definitions specified in Sec. 173.115.

(2) Any mixture having one or more components with a flash point of 60.5 [deg]C (141 [deg]F) or higher, that make up at least 99 percent of the total volume of the mixture, if the mixture is not offered for transportation or transported at or above its flash point.

(3) Any liquid with a flash point greater than 35 [deg]C (95 [deg]F) that does not sustain combustion according to ASTM D 4206 (IBR, see Sec. 171.7 of this subchapter) or the procedure in appendix H of this part.

(4) Any liquid with a flash point greater than 35 [deg]C (95 [deg]F) and with a fire point greater than 100 [deg]C (212 [deg]F) according to ISO 2592 (IBR, see Sec. 171.7 of this subchapter).

(5) Any liquid with a flash point greater than 35 [deg]C (95 [deg]F) which is in a water-miscible solution with a water content of more than 90 percent by mass.

(b) Combustible liquid. (1) For the purpose of this subchapter, a combustible liquid means any liquid that does not meet the **definition** of any other hazard class specified in this subchapter and has a flash point above 60.5 [deg]C (141 [deg]F) and below 93 [deg]C (200 [deg]F).

(2) A **flammable** liquid with a flash point at or above 38 [deg]C (100 [deg]F) that does not meet the **definition** of any other hazard class may be reclassed as a combustible liquid. This provision does not apply to transportation by vessel or aircraft, except where other means of transportation is impracticable. An elevated temperature material that meets the **definition** of a Class 3 material because it is intentionally heated and offered for transportation or transported at or above its flash point may not be reclassed as a combustible liquid.

(3) A combustible liquid that does not sustain combustion is not subject to the requirements of this subchapter as a combustible liquid. Either the test method specified in ASTM D 4206 or the procedure in appendix H of this part may be used to determine if a material sustains

combustion when heated under test conditions and exposed to an external source of flame.

(c) Flash point. (1) Flash point means the minimum temperature at which a liquid gives off vapor within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid. It shall be determined as follows:

(i) For a homogeneous, single-phase, liquid having a viscosity less than 45 S.U.S. at 38 [deg]C (100 [deg]F) that does not form a surface film while under test, one of the following test procedures shall be used:

(A) Standard Method of Test for Flash Point by Tag Closed Tester, (ASTM D 56);

(B) Standard Methods of Test for Flash Point of Liquids by Setaflash
Closed Tester, (ASTM D 3278); or

(C) Standard Test Methods for Flash Point by Small Scale Closed Tester, (ASTM D 3828).

(ii) For a liquid other than one meeting all of the criteria of paragraph (c)(1)(i) of this section, one of the following test procedures shall be used:

(A) Standard Method of Test for Flash Point by Pensky--Martens Closed Tester, (ASTM D 93). For cutback asphalt, use Method B of ASTM D 93 or alternate tests authorized in this standard; or

(B) Standard Methods of Test for Flash Point of Liquids by Setaflash
Closed Tester (ASTM D 3278).

(2) For a liquid that is a mixture of compounds that have different volatility and flash points, its flash point shall be determined as specified in

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paragraph (c)(1) of this section, on the material in the form in which it is to be shipped. If it is determined by this test that the flash point is higher than -7 [deg]C (20 [deg]F) a second test shall be made as follows: a portion of the mixture shall be placed in an open beaker (or similar container) of such dimensions that the height of the liquid can be adjusted so that the ratio of the volume of the liquid to the exposed surface area is 6 to one. The liquid shall be allowed to evaporate under ambient pressure and temperature (20 to 25 [deg]C (68 to
77 [deg]F)) for a period of 4 hours or until 10 percent by volume has evaporated, whichever comes first. A flash point is then run on a portion of the liquid remaining in the evaporation container and the lower of the two flash points shall be the flash point of the material.

(3) For flash point determinations by Setaflash closed tester, the glass syringe specified need not be used as the method of measurement of
the test sample if a minimum quantity of 2 mL (0.1 ounce) is assured in the test cup.

(d) If experience or other data indicate that the hazard of a material is greater or less than indicated by the criteria specified in paragraphs (a) and (b) of this section, the Associate Administrator may revise the classification or make the material subject or not subject to
the requirements of parts 170-189 of this subchapter.

[Amdt. 173-224, 55 FR 52634 Dec. 21, 1990, as amended by Amdt. 173-227, 56 FR 49989, Oct. 2, 1991; 56 FR 66268, Dec. 20, 1991; 57 FR 45461, Oct.
1, 1992; Amdt. 173-241, 59 FR 67506, 67507, Dec. 29, 1994; Amdt. 173-255, 61 FR 50625, Sept. 26, 1996; Amdt. 173-261, 62 FR 24731, May 6, 1997; 66 FR 45379, 45381, Aug. 28, 2001; 68 FR 75743, Dec. 31, 2003]

APPENDIX C

Material Safety Data Sheet

Infosafe No. NU003 Issue Date: January 2002 ISSUED by NUFARM

Product Name: **AF300 Herbicide**

Classified as hazardous according to criteria of NOHSC

COMPANY DETAILS

Company Name	NUFARM AUSTRALIA LIMITED. (ABN 80 004 377 780)
Address	103-105 Pipe Road Laverton North Victoria 3026 Australia
Emergency Tel.	24hr 1800 033 498
Tel/Fax	Tel: (03) 9282-1000 Fax: (03) 9282-1001
Other Information	

IDENTIFICATION

Product Code	0027
Product Name	AF300 Herbicide
Proper Shipping Name	FLAMMABLE LIQUIDS, N.O.S. - (2,4-dichlorophenoxyacetic acid/kerosine)
UN Number	1993
DG Class	3
Packing Group	III
Hazchem Code	2Y
Poisons Schedule	S5
Product Use	For the integrated control of Groundsel bush, Mother-of-millions, Noogoora burr, Bathurst burr and water hyacinth and other weeds as listed in the Directions for Use Table.

Physical Data

Appearance	Light straw coloured limid liquid with typical hydrocarbon odour.
Melting Point	<0°C
Boiling Point	>160°C (for solvent)
Vapour Pressure	Active ingredient considered non-volatile
Specific Gravity	1.03 - 1.05 (1.044)
Flash Point	40°C
Flamm. Limit LEL	No information available

Other Properties

Volatile Component	~23%
Autoignition Temp.	No information available
Vapour Density	No information available
Form	Liquid
Other Information	Emulsifies in water.

Ingredients

Ingredients	Name	CAS	Proportion
	2,4-Dichlorophenoxy acetic acid	94-75-7	300 g/L
	Synthetic ethoxylated alcohol	68439-46-3	50 %
	Solvent 400		235 g/L

HEALTH HAZARD INFORMATION

Health Effects

Acute - Swallowed A significant hazard exists if the concentrate is accidently swallowed. Absorption of relatively large amounts of 2,4-D can produce headaches, nausea, lethargy, motor weakness and inco-ordination
The concentrate is considered harmful if swallowed, when classified according to the Worksafe Criteria.

Classified as hazardous according to criteria of NOHSC

Acute - Eye	The concentrate is irritating to the eyes. No permanent effects on the eyes is expected from a single exposure
Acute - Skin	The concentrate is irritating to the skin. Prolonged or repeated exposure may cause defatting of the skin which could lead to secondary dermatitis. Some absorption of 2,4-D acid is possible if contact with the concentrate is prolonged.
Acute - Inhaled	Inhalation of solvent may lead to headache or nausea if exposure is prolonged. Avoid breathing spray mists.
Chronic	Chronic Over Exposure: Repeated absorption of relatively large doses of 2,4-D presents a risk to the liver and kidneys.
Other Information	If poisoning occurs, contact a Doctor or Poisons Information Centre 13 11 26

First Aid

Swallowed	If swallowed do NOT induce vomiting; seek medical advice immediately and show this container or label or contact the Poisons Information Centre on 13 11 26. Make every effort to prevent vomit from entering the lungs by careful placement of the patient. The above first aid instructions are mandated by the Commonwealth Department of Health and Aged Care via the National Drugs and Poisons Schedule. These instructions are suitable for ingestion of spray solution and small amounts of concentrate; however, if SUBSTANTIAL AMOUNTS of the concentrate have been swallowed (more than about 50ml) AND if medical assistance is more than 30 minutes away, the induction of vomiting should be CONSIDERED, preferably based on MEDICAL ADVICE if a physician can be contacted by phone. All care must be taken to prevent vomit from being inhaled. Do not give anything by mouth to a semi-consious or unconscious person.
Eye	Immediately irrigate with copious quantity of water for at least 15 minutes. Eyelids to be held open.
Skin	Wash affected areas throughly with soap and water. Remove contaminated clothing and launder before re-use.
Inhaled	Remove victim to fresh air until recovered.

Advice to Doctor

Advice to Doctor	Treat symptomatically. Aspiration of vomitus may lead to pulmonary pneumonitis, which may be serious, especially in young children.

Other Health Hazard Information

PRECAUTIONS FOR USE

Exposure Limits	No exposure limits have been set for this product, however, an exposure limit has been set for 2,4-D acid (solid) at 10 mg/m3
Eng. Controls	Handle the concentrate in a well ventilated space. Natural ventilation is adequate, although a local exhaust should be provided if material is handled in confined spaces.

Personal Protection

Protective Equip.	Avoid contact with eyes and skin. DO NOT inhale spray mist. When preparing spray wear PVC or rubber apron, elbow-length PVC gloves and face shield. When using the prepared spray wear face shield. If product on skin, immediately wash area with soap and water. After use and before eating, drinking and smoking, wash hands, arms and face thoroughly with soap and water. After each day's use, wash gloves, face shield and contaminated clothing.

Flammability

Infosafe No. NU003 Issue Date : January 2002 ISSUED by NUFARM

Product Name : **AF300 Herbicide**

Classified as hazardous according to criteria of NOHSC

Fire Hazards	Flammable 40°C (Abel L.C.) for solvent present.

SAFE HANDLING INFORMATION

Storage and Transport

Storage and Transport	Transport Details: Proper Shipping Name: Flammable liquid, n.o.s. (2,4-dichlorophenoxyacetic acid) UN No. 1993 Class: 3 Packaging Group: III Hazchem: 2Y FLAMMABLE Avoid all sources of ignition including static electricity buildup during transfer operations. Store in original container, tightly sealed, in a safe place away from seeds, fungicidal and insecticidal sprays or ferilizers.
Proper Shipping Name	FLAMMABLE LIQUIDS, N.O.S. - (2,4-dichlorophenoxyacetic acid/kerosine)
EPG Number	3A1

Spills and Disposal

Spills & Disposal	Contain spill and absorb with sand or proprietary absorbent (vermiculite). Prevent from entering drains, waterways or sewers. Collect in sealed open top containers for disposal. Triple rinse containers, add rinsate to the spray tank, then offer container for recycling/reconditioning, or puncture top, sides and bottom and dispose of in landfill in accordance with local regulations. On-site disposal of concentrate is not acceptable.

Fire/Explosion Hazard

Fire/Explos. Hazard	Extinguishing Media: Water fog, dry chemical, foam, CO2. Special Fire Fighting Procedures: Breathable air apparatus may have to be worn if material is involved in fires especially in confined spaces. Keep upwind. Unusual Fire and Exposion Hazard: May emit toxic fumes of hydrogen chloride, phosgene and carbon monoxide if material is involved in fires or subjected to extreme heat.
Hazardous Reaction	Store away from oxidising agents, may react violently with strong oxidising agents. Polymerisation is not possible.
Hazchem Code	2Y

OTHER INFORMATION

Nufarm

Material Safety Data Sheet

Infosafe No. NU003 Issue Date : January 2002 ISSUED by NUFARM

Product Name : **AF300 Herbicide**

Classified as hazardous according to criteria of NOHSC

Toxicology

2,4-D (2,4-dichlorphenoxyacetic acid)
LD50 (oral, rat): 699mg/Kg
LD50 (dermal, rabbit): >2,000mg/Kg
LC50 (inhalation, rat): >1.79mg/L (4hr)(maximum attainable concentration)
Not toxic to bees
LC50 (rainbow trout): ~100mg/L
LC50 (daphnia): 1.4mg/L
LC50 (mallard duck): >5,000mg/Kg diet
In trials using 2,4-D as a drug, studies on volunteers have shown that doses of between 5 and 36mg/Kg body weight do not cause any acute toxic effects. Formulated 2,4-D products can be absorbed by ingestion, inhalation (spray mist) and through the skin. Studies of users (sprayers) has shown that absorption through the skin is the most common route. When used with good agricultural spraying practice and good personal hygiene, absorption of 2,4-D is very low.
2,4-D does not accumulate in the body; a single dose of 2,4-D is rapidly excreted (in a few days), mainly in the urine.
The Australian Acceptable Daily Intake(ADI) of 2,4-D for a human is 0.01mg/kg/day, set for the public for daily, lifetime exposure. This is based on the NOEL of 1.0mg/kg/day, the level determined to show no effects during long term exposure for the most sensitive indicators and the most sensitive species. (Ref: Comm. Dept. of Health and Aged Care, 'ADI List', TGA, August 2001).

Environ. Protection

2,4-D products do not appear to pose any threat to birds.
2,4-D products do not appear to pose any threat to fish other than in very hign concentrations.
DO NOT spray in high winds. Do not contaminate dams, waterways or streams with this product or used containers. DO NOT use this container for any other purpose. After use, triple rinse containers, add rinsate to the spray tank, then offer container for recycling/reconditioning, or pucture top, sides and bottom and dispose of in landfill in accordance with local regulations. On-site disposal of concentrate is not acceptable.
Equipment that has been used for this product should not be used for the application of other materials to sensitive plants, unless it has been well washed out with hot, soapy water or 1% ammonia solution, followed by several clear water rinses.
Do not use on or in situations were damage to susceptible crop plants such as cotton, tobacco, tomatoes, flowers, vines fruit trees or other susceptible crop plants may result from direct application or spray drift.

Nufarm

Material Safety Data Sheet

Infosafe No.	NU003	Issue Date: January 2002	ISSUED by NUFARM

Product Name : **AF300 Herbicide**

Classified as hazardous according to criteria of NOHSC

Pkg. & Labelling

WARNING
KEEP OUT OF REACH OF CHILDREN
READ SAFETY DIRECTIONS BEFORE OPENING
Not to be used for any purpose or in any manner contrary to the label unless authorised under appropriate legislation.
The product has been assessed according to the Worksafe criteria for classifying hazardous substances and is classified as hazardous:
Risk Phrases:
R10 Flammable
R22 Harmful if swallowed
R36/37/38 Irritating to eyes, respiratory system and skin
R65 Harmful: may cause lung damage if swallowed
Safety Phrases:
S2 Keep out of reach of children
S23 Do not breathe vapour
S24 Avoid contact with skin
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S36/37 Wear suitable protective clothing and gloves
S62 If swallowed, do not induce vomiting; seek medical advice immediately and show this container or label. Refer to First Aid section.

CONTACT POINT

Contact

Normal Hours: Mr Volker Maier Phone: (03) 9282 1000
After Hours: Shift Supervisor Phone: 1800 033 498

...End Of MSDS...

APPENDIX 2

C9-11 Pareth-3
RN: 68439-46-3

Name of Substance
C9-11 Pareth-3
C9-11 Pareth-6
C9-11 Pareth-8
Pareth-91-3
Pareth-91-6
Pareth-91-8

Synonyms
(C9-C11) Alkyl alcohol, ethoxylate
(C9-C11)Alkyl alcohol ethoxylate
Neodol 91-6
Polyethylene glycol, nonyl, decyl, undecyl ether

Systematic Name
Alcohols, C9-11, ethoxylated
Alkyl(C9-11) alcohol, ethoxylated

Superlist Name
Alcohols, C9-11, ethoxylated

Auxiliaries for agrochemical formulations

RHÔNE-POULENC

RHÔNE-POULENC GERONAZZO S.p.A.

3-1 AQUEOUS SOLUTIONS —

Some active ingredients, which are readily soluble and chemically stable in water can be formulated as concentrated solutions. That is the simpliest and the cheapest type of formulation.
However some possible problems needs to be considered:

- the solubility of the active ingredient in the formulation have to be sufficiently high to avoid crystallisation during storage at low temperature.
- The solution diluted at the use rate needs to have a wetting effect on the foliage.

For these reasons to the AQUEOUS SOLUTIONS are often added solubilising agents to improve the solubility at low temperature and sufactants to improve the wetting effect and the penetration of the active ingredient through the cuticular layer.
The wetting agents in our production range are the following:

- **SOPROPHOR 860/P**
- **SOPROPHOR 840**
- **SOPROPHOR BC/10**

As penetration improvers we have:

- **SOPROMINE S/30**
- **SOPROMINE S/35**
- **SOPROMINE O/15**
- **SOPROMINE O/20**

Some more information is given in the chapter: «IMPROVEMENT OF PENETRATION OF CUTICULAR LAYER BY SURFACTANTS» (4.2).

3-2 EMULSIFIABLE CONCENTRATES —

Emulsifiable concentrates, have always been widely used because of their rather simple manufacture process.
Emulsifiable concentrates usually contain:

- active ingredients
- emulsifiers
- stabilizers, stickers, pH buffer etc...
- solvents and cosolvents

The most usual solvents are xylene (usage of this product is now restricted in a number of countries), aromatic solvents such as SOLVESSO, SHELLSOL, etc.
Sometimes to improve the solubility of the active at low temperature it's necessary to add polar solvents such as cyclohexanone, dimethyl-formamide or isophorone etc...

For the application in the field, such a formulation is diluted in water, forming usually an oil-in-water emulsion which permits a uniform distribution of active ingredients on the crop.
The performance of an emulsifier in E.C. is very important to guarantee dispersed phase droplets in the range of O.1. to 5 microns and ensure uniform spreading and wetting which is essential for efficiency. E.C. must always be in compliance with international specifications: F.A.O. (according to CIPAC methods) and W.H.O. They must also be in compliance with those specifically applied in every single country or by every single customer, as long as they respect the under mentioned chemical-physical characteristics:

1) Stability in the long term (2 years approx).
2) Heat stability (54° C).
3) Cold stability (0° C).

When diluted into water, they must have the following characteristics:

1) Good blooming.
2) Good stability to creaming, no oil separation.
3) Behave satisfactorily in water of different hardnesses and temperatures.
4) Perform to the field conditions (different use rates on the field).

3-2-1 EMULSIFIERS RANGE

We list our range of emulsifiers as:

- base emulsifiers.
- blended emulsifiers.

a) *Base emulsifiers*

These are single surfactants, used as a mixture of one or more hydrophilic nonionic surfactants with a lipophilic anionic one. Their balancing is quite critical and the ratios of emulsifiers strictly applied.
Our main base emulsifiers are:

- **NONIONIC**
  - **SOPROPHOR B**
  - **SOPROPHOR OR/36**
  - **SOPROPHOR BSU**
  - **SOPROPHOR S/25**
  - **SOPROPHOR 461/P**
  - **SOPROPHOR 487/P**
  - **SOPROPHOR 497/P**
  - **SOPROPHOR 724/P**

- **ANIONIC**

  - **SOPROPHOR 70**
  - **SOPROPHOR 70/B**
  - **SOPROPHOR 60/BE**
  - **SOPROPHOR 2283**

b) *Blended emulsifiers*

These are blends of anionic and nonionic surfactants, usually with relatively close HLB, used as pairs. Because of their particular compositions, with two or more tensides, their balance is easier and consequently, they offer a wider application field. Blended emulsifiers are also used for some specific formulations which are very difficult to achieve with base emulsifiers.
The main blended emulsifiers we offer are:

Lipophilic activity

- **GERONOL FF/4**
- **GERONOL SC/121**

Hydrophilic activity

- **GERONOL MS**
- **GERONOL FF/6**
- **GERONOL RE/70**
- **GERONOL V/497**
- **GERONOL V/87**

We also developped a similar range of products with a flash point higher than 65° C:

Lipophilic activity

- **GERONOL FF/4-E**
- **GERONOL SC/121-E**

Hydrophilic activity

- **GERONOL MS-E**
- **GERONOL FF/6-E**
- **GERONOL RE/70-E**
- **GERONOL V/497-E**
- **GERONOL V/87-E**

3-2-2 SCREENING OF THE SUITABLE EMULSIFIERS

There are two methods:

3-2-2-1 Practical method based on direct research

According to the following scheme that shows the initial preferential couplings, in relation to their well-known multipurpose activity, prepare:

a) system to emulsify (active ingredients, solvents and stabilizers), containing 5% of a surfactant of table 1.
b) system to emulsify (active ingredients, solvents and stabilizers), containing 5% of a surfactant of table 2.
c) Mix the two solutions according to the known method:

a) system:	10	20	30	40	50	60	70	80	90
b) system:	90	80	70	60	50	40	30	20	10

Find the best balance in order to have a good blooming and consequently good stability to creaming and no oil separation.
If the results are not satisfactory, repeat the test with another nonionic until the suitable pair is found.
Verify eventually, the best ratio of balancing reducing the range of control to 5% (5:95/ 10:90/ 15:85 and so on) instead of 10% as mentioned above.
In some specific cases, it may be necessary to use more than 5% emulsifier to obtain the requested performances.
Increasing the emulsifiers contents provide a better resistance to ageing and reduce variations in performance due to changeable chemical physical characteristics of the components.

— EMULSIFIERS SCREENING SCHEME —

TABLE I	TABLE II
Anionics	*Nonionics*
(Lipophilic activity)	*(Hydrophilic activity)*
BLENDS	
GERONOL FF/4	GERONOL MS
	GERONOL FF/6
	GERONOL RE/70
	GERONOL V/497
BASES	
SOPROPHOR 70	SOPROPHOR OR/36
SOPROPHOR 70/B	SOPROPHOR S/25
SOPROPHOR 2283	SOPROPHOR 497/P
	SOPROPHOR 724/P

The use of above mentioned products usually solves most of the E.C. formulation problems.
Other surfactants (shown in the list of paragraph «Emulsifiers range») could be taken into account, if some particular emulsivity problems occur.
SOPROPHOR 60/BE (alkylaryl sulphonate calcium salt — non flammable) is used mixed with «base emulsifiers» when E.C. with a high flash point is required.
SOPROPHOR 70 (branched) has similar activity of the SOPROPHOR 70/B (linear) and may replace it if the norms of the country allow its utilization.

3-2-2-2 By the HLB determination (HLB system)

It is a long time since the HLB system (hydrophilic-lipophilic balance) was introduced and used, providing reasonable results.
Many specifications and discussions could take place on this principle, also considering the great number of publications issued upon the subject, but its utilisation may be shortly summarised as follows: one should bear in mind that a certain knowledge of the surfactants and of the systems to emulsify is needed in order to use it properly.

a) *Notes on the HLB system*

An arbitrary scale of HLB values is usually abscribed to emulsifiers, ranging from 0 to 20, assuming from 0 to 10 for the lipophil tendency, and from 10 to 20 for the hydrophil tendency.
By using two emulsifiers with a well-known HLB (SOPROPHOR S/25 - SOPROPHOR 70) the HLB of the system to emulsify is determined.
By balancing the surfactants of the «Emulsifiers range» so as to obtain the same HLB, one will find the pair giving the best emulsivity results, which however depend on many factors.

b) *HLB determination of the concentrate to emulsify*

Prepare two solutions having the same E.C. taken into account, the former containing 7% of SOPROPHOR S/25, the latter containing 7% of SOPROPHOR 70, being the most universal matched pair.
Find the best ratio of emulsifier corresponding to the best emulsifiability, in order to determine the optimum HLB.
For this practical research one uses the method cited in «Screening of the suitable emulsifiers» (paragraph 3-2-2-1).
The HLB value is calculated in the following way:

Example:

SOPROPHOR S/25	(HLB 14,5)	- 50%	×	14,5	=	7.25
SOPROPHOR 70	(HLB 8,5)	- 50%	×	8,5	=	4.25

HLB of the mixture 11.50

c) *Determination of the HLB of surface active agents*

There are a number of prescribed methods for rapid theoretical determination of the HLB from knowledge of the molecular structure, e.g.:

$$HLB = \frac{H}{5}$$

«H» being the relative percentage by weight of the hydrophilic moiety in the molecule.

$$HLB = 20\ (1 - \frac{IS}{IA})$$ (valid for ethoxylated fatty acids)

«IS» being the saponification value of the nonionic.
«IA» being the acid value of the fatty acid.
These two formulas can easily be combined.
DAVIES treated the HLB value as a sum of structural factors, each group in the molecule bringing its own contribution to the total HLB value. The following equation allows a good approximation of HLB for most surface active agents.

HLB = 7 + E (Hydrophilic group)—C (lipophilic group).

To have a better chance of obtaining good emulsion, it is advisable to select a surfactant with an HLB value as close as possible to that of the phase to be dispersed.
To give an example, HLB values of several well-known products are shown below.

Disperse phase	*HLB*	*Disperse phase*	*HLB*
Paraffinic oil	10	Solvent naphta	14
Mineral oil	11.5	Benzene	15
Vaseline	12	Diisopropylbenzene	15
Orthodichlorobenzene	13	Toluene	16
Kerosene	14	Pine oil	16
Xylene	14	Essential oils	15-17

3-2-3 CONTROL METHODS

There are different control methods existing, which some large manufacturers and countries usually refer to, in compliance with the particular environmental and legislative requirements.
The formulations listed in this catalogue have been specifically designed in order to achieve the best performances by using the official CIPAC control methods which, on average, better summarise the different norms.
The qualitative specifications which the E.C. must show, can be generally summarised and simplified as follows:

1) Limpid product, without suspended matter or sediment.
2) Active ingredient content.
3) Emulsion stability and re-emulsion: (CIPAC 1-MT 36).
4) pH: (CIPAC 1-MT 75).
5) Storage: low temperature stability: (CIPAC 1-MT 39).
high » » (CIPAC 1-MT 46.1.3).

The formulations subjected to accelerated storage test by heating might show slight chemical-physical variations to items 1, 2, 3, 4 and, however, comply with the FAO specifications or close values when not edited.
Better performances could be achieved with components of changeable chemical-physical characteristics, water with different hardnesses and temperatures, by balancing the ratios of the emulsifiers.

EMULSIFIABLE CONCENTRATES - 3.2

Active Ingredients		Emulsifiers						Stabilizers and solvents		
		FF/4	FF/6	MS	V/497	V/87	---	---	Xylene	Shellsol ab
Acetochlor	50	2,5				4,0		MCB. up to 100		
Alachlor	48	2,2				2,8		MCB. up to 100		
Azinphos Ethyl	20	2,0		3,0					up to 100	
Azinphos Methyl	20	1,0		8,0				MCB. up to 100		
Butachlor	60	4,0	2,0						up to 100	
Carbophenothion	46	3,6			2,4				up to 100	
Chlorfenson	30	2,5	7,5						up to 100	
Chlordane	75	5,8				4,2		EPO. 1	up to 100	
Chlorobenzilate	50	1,6		4,5					up to 100	
Chlorpyrifos Ethyl	48	3,2					RE/70 1,8		up to 100	
Cypermethrin	10	2,7		3,3					up to 100	
Cypermethrin	25	3,0		3,0					up to 100	
Cypermethrin	10	3,3		2,7						up to 100
Cypermethrin	25	3,6		2,4						up to 100
Diazinon	60	3,0		2,4				EPO. 2	up to 100	
Dichlorvos	50				3,7		OR/36 : 2,3	EPO. 2	up to 100	
Dicofol	18,5	0,7		6,3					up to 100	
Dicofol	48	2,6				9,4		Cyclohexanone 26	up to 100	
Dicofol/Tetradifon	16/6	0,6		5,4					up to 100	
Dimethoate	40						SC/167 : 5,0	Cyclohexanone 40	up to 100	
Dinocap	48	1,0		4,0					up to 100	
2-4 D Isooctyl Ester	50	1,7		3,3						up to 100

PURDUE PESTICIDE PROGRAMS
Purdue University Cooperative Extension Service

PESTICIDES AND FORMULATION TECHNOLOGY

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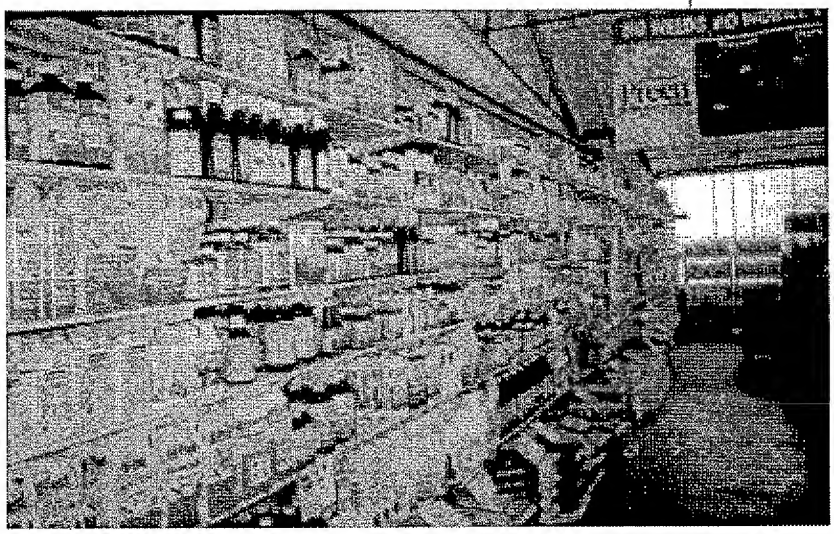
PESTICIDE PRODUCTS AND THE MODERN MARKETPLACE

There is a seemingly endless variety of pesticide products sold in the urban and agricultural marketplace. Casual observation in any hardware store or lawn and garden center will reveal that variations extend even to products that are manufactured by the same chemical company and contain the same ingredients.



Manufacturers often produce various forms of a pesticide to meet different pest control needs. For example, an insecticide may be applied as a liquid to control adult Japanese beetles on rose bushes and as a solid material for suppressing the larval (grub) stage of that insect in turf. Applying the insecticide as a liquid spray permits contact with the adult beetle, while the solid form can be watered into the root zone of the lawn where the grubs live.

A pesticide product consists of two parts: active and inert ingredients. Active ingredients are chemicals which actually control the pest. Inert ingredients are primarily solvents and carriers that help deliver the active ingredients to the target pest; they serve to enhance the utility of the product. Inert ingredients may be liquids into which the active ingredient is dissolved, chemicals that keep the product from separating or settling, and even compounds that help secure the pesticide to its target after application.

The combination of an active ingredient with a compatible inert ingredient is referred to as a formulation. Pesticides are formulated for a number of

different reasons. A pesticide active ingredient in a relatively pure form, ready for manufacturer's use, rarely is suitable for field application. An active ingredient usually must be formulated in a manner that

- increases pesticide effectiveness in the field
- improves safety features
- enhances handling qualities

The formulation gives the product its unique physical form and specific characteristics, enabling it to fill a market niche. There are approximately 860 pesticide active ingredients formulated into 21,000 pesticide products sold and used in the United States today. For most practical purposes, the terms *formulation* and *product* can be used interchangeably.

AN OVERVIEW OF THE FORMULATION PROCESS

The active ingredients in pesticide products come from many sources. Some, such as nicotine, pyrethrum, and rotenone, are extracted from plants. Others have a mineral origin, while a few are derived from microbes. However, the vast majority of active ingredients are synthesized in the laboratory. These synthetic active ingredients may have been designed by an organic chemist or discovered through a screening process of chemicals generated by various industries.

Regardless of their source, pesticide active ingredients have different solubilities. Some dissolve readily in water, others only in oils. Some active ingredients may be relatively insoluble in either water or oils. These different solubility characteristics, coupled with the intended use of the pesticide, in large measure define the types of formulations in which the active ingredient may be delivered.

It is preferable from the manufacturer's perspective to use the active ingredient in original form, when possible (e.g., a water soluble active ingredient formulated as a water soluble concentrate). When this is not feasible, it may become necessary to alter the active ingredient in order to change its solubility characteristics. This would be done, obviously, in a manner that did not detract from the pesticidal properties of the active ingredient.

Usually, an active ingredient will be combined with appropriate inert materials prior to packaging. A brief review of some basic chemistry terminology should prove helpful in understanding differences among the various types of formulations.

Example: 2,4-D

The herbicide 2,4-D (2,4-dichlorophenoxyacetic acid), in purified form, is a white, crystalline solid. It is an organic acid that is not particularly soluble in water or oil. For this reason, the acid form of 2,4-D has not seen much use in commercially available products.

Generally, the acid form of 2,4-D is combined with a base. Bases neutralize acids and the resulting product is a salt and water. In this case, a salt of 2,4-D is generated. Most salts of 2,4-D are water soluble.

Finally, the acid form of 2,4-D can be combined with an alcohol to create a 2,4-D ester; 2,4-D esters are oil soluble liquids.

In this manner, the herbicide 2,4-D can be altered to change its solubility characteristics and ultimately permit the development of a number of formulations far beyond those available through the use of the acid form.

Sorption

In some cases it may be necessary or desirable to adhere a liquid active ingredient onto a solid surface (e.g., a powder, dust, or granule). This process is called *sorption* and it can be accomplished by two possible mechanisms:

- Adsorption—a chemical/physical attraction between the active ingredient and the surface of the solid.
- Absorption—entry of the active ingredient into the pores of the solid.

Solution

A solution results when a substance (the solute) is *dissolved* in a liquid (the solvent). The solute can be a solid, a liquid, or a gas. The components of a true solution cannot be mechanically separated. Once mixed, a true solution does not require agitation to keep its various parts from settling. Solutions are frequently transparent, although if they are darkly colored this may not be the case. An example of a solution is the active ingredient in the herbicide Gramoxone®: paraquat (solute) dissolved in water (solvent).

Suspension

A suspension is a mixture of finely divided, solid particles *dispersed* in a liquid. The solid particles do not dissolve in the liquid, and the mixture must be agitated to maintain thorough distribution. Most suspensions will have a cloudy appearance. The herbicide AAtrex 4L® is formulated as a suspension. The label directs the user to shake well before using. This product also forms a suspension when mixed with water for application as a spray. Explicit label information describes the need for sufficient agitation to keep the product dispersed in the spray tank.

Emulsion

An emulsion is a mixture that occurs when one liquid is *dispersed* (as droplets) in another liquid. Each liquid will retain its original identity and some degree of agitation generally is required to keep the emulsion from separating. Emulsions usually will have a "milky" appearance. The insecticide Diazinon 4E® is formulated as an emulsifiable concentrate. The active ingredient is dissolved in an oil-based solvent. When the product is mixed with water, an emulsion is formed. An emulsifying agent in the formulated product helps prevent the emulsion from separating by surrounding the oil droplets that contain the dissolved active ingredient to keep them from reuniting.

Familiarity with the different terms and processes described above will lead to a greater understanding and appreciation of the advantages and disadvantages of many commonly used pesticide formulations.

COMMON PESTICIDE FORMULATIONS AND SELECTION CONSIDERATIONS

The importance of formulation type is generally overlooked. A well-considered decision to use the most appropriate formulation for a given application will include an analysis of the following factors:

- **Applicator safety.** Different formulations present various degrees of hazard to the applicator. Some products are easily inhaled, while others readily penetrate skin, or cause injury when splashed in the eyes.
- **Environmental concerns.** Special precautions need to be taken with formulations that are prone to drift in air or move off target into water. Wildlife can also be affected to varying degrees by different formulations. Birds may be attracted by granules, and fish or aquatic invertebrates can prove especially sensitive to specific pesticide formulations such as 2,4-D esters.
- **Pest biology.** The growth habits and survival strategies of a pest will often determine what formulation provides optimum contact between the active ingredient and the pest.
- **Available application equipment.** Some pesticide formulations require specialized application equipment. This includes safety equipment, spill control equipment and, in special cases, containment structures.
- **Surfaces to be protected.** Applicators must be aware that certain formulations can stain fabrics, discolor linoleum, dissolve plastic, or burn foliage.

• **Cost.** Product prices may vary substantially, based on the ingredients used and the complexity of delivering active ingredients in specific formulations.

Individuals such as commercial pest control technicians or farmworkers who may not be involved in the selection process but are responsible for the actual application should also be very aware of the type of formulation they are using. As stated, formulation type can have an impact on hazards to human health and the environment. Inattention to the type of formulation being used could mean the difference between a routine application and one that is the source of environmental contamination—or worse, a serious human exposure.

Formulations are classified as solids or liquids on the basis of their physical state in the container at the time of purchase. A formulation can contain more than one active ingredient, and many have to be further diluted with an appropriate carrier (e.g., water) prior to use.

Solid Formulations

Solid formulations can be divided into two types: ready-to-use, and concentrates which must be mixed with water to be applied as a spray. The properties of six solid formulations are described in this publication. Three of the solid formulations (dusts, granules, and pellets) are ready-to-use, and three (wettable powders, dry flowables, and soluble powders) are intended to be mixed with water.

Dusts

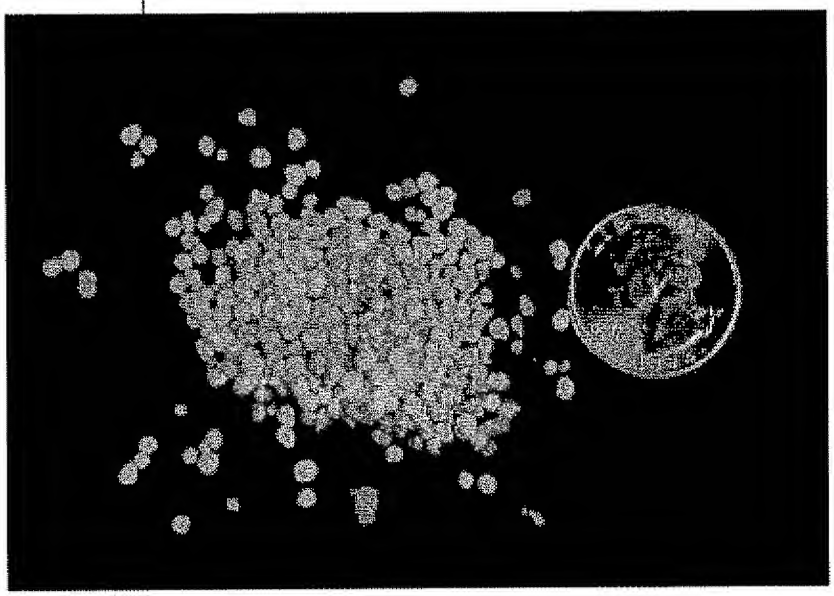
Dusts are manufactured by the sorption of an active ingredient onto a finely-ground, solid inert such as talc,

Dust

clay, or chalk. They are relatively easy to use because no mixing is required and the application equipment (e.g., hand bellows and bulb dusters) is lightweight and simple. Dusts can provide excellent coverage, but the small particle size that allows for this advantage also creates an inhalation and drift hazard. In general, dust formulations are no longer used in large scale outdoor situations due to their high drift potential. However, dusts are still applied as spot treatments for insect and disease control outside. Commercial pest control operators use dusts effectively in residential and institutional settings for control of various insect pests. Indoors, this type of formulation permits the delivery of an insecticide into cracks and crevices, behind baseboards and cabinets, etc. Thus, the insecticide is placed into the pest's habitat and away from contact by people and pets.

Granules

The manufacture of granular formulations is similar to that of dusts except that the active ingredient is sorbed onto a larger particle. The inert solid may be clay, sand, or ground plant materials. A granule is defined by size: Granule-sized products will pass through a 4-mesh (number of wires per inch) sieve and be retained on an 80-mesh sieve. Granules are applied dry and usually are intended for soil applications where they have the advantage of weight to carry them through foliage to the ground below. The larger particle size of granules, relative to dusts, minimizes the potential for drift. There is also a reduced inhalation hazard, but fines are associated with the formulation—especially when a bag is being emptied. In addition, granules have a low dermal hazard. The primary drawbacks of granules are their bulk, the problems they



Granules

present in handling, and the difficulty inherent in achieving a uniform application with this type of product. Granules also may have to be incorporated into the soil to work, and they are sometimes attractive to nontarget organisms such as birds.

Pellets

Pellets are very similar to granules, but their manufacture is different. The active ingredient is combined with inert materials to form a slurry (a thick liquid mixture). This slurry is then extruded under pressure through a die and cut at desired lengths to produce a particle that is relatively uniform in size and shape. Pellets are typically used in spot applications. Pelleted formulations provide a high degree of safety to the applicator. They do have the potential to roll on steep

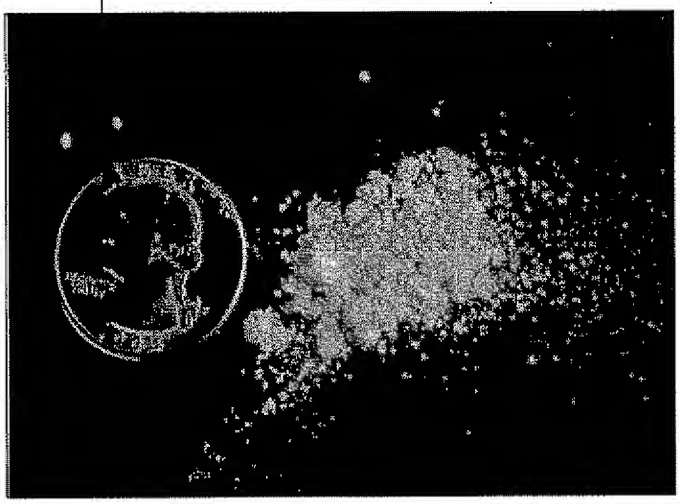
Pellets

or frozen slopes and thereby harm nontarget vegetation or contaminate surface water.

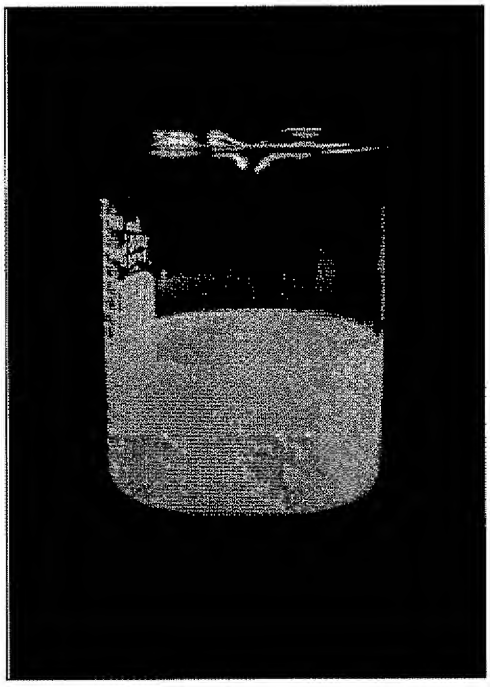
Wettable Powders

Wettable powders are finely divided solids, typically mineral clays, to which an active ingredient is sorbed. This formulation is diluted with water and applied as a liquid spray. Upon dilution, a suspension is formed in the spray tank. Wettable powders will likely contain wetting and dispersing agents as part of the formulation. These are chemicals used to help wet the powder and disperse it throughout the tank. Wettable powders are a very common type of formulation. They provide an ideal way to apply an active ingredient in spray form that is not readily soluble in water. Wettable powders tend to pose a lower dermal hazard in comparison to

liquid formulations, and they do not burn vegetation as readily as many oil-based formulations. This formulation does present an inhalation hazard to the applicator during mixing and loading because of the powdery nature of the particles. Furthermore, there are a series of disadvantages associated with *all* formulations that form a suspension in the spray tank: They require agitation to prevent settling out; they can be abrasive to equipment; and they may cause strainers and screens to plug.



Wettable powder before mixing

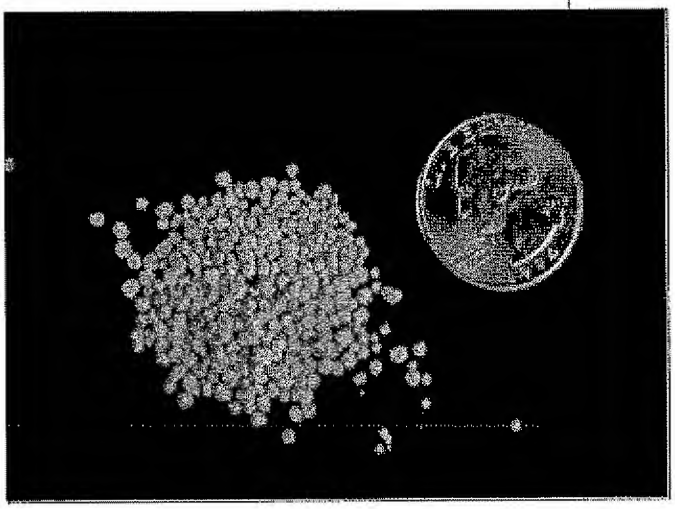


Wettable powder after mixing

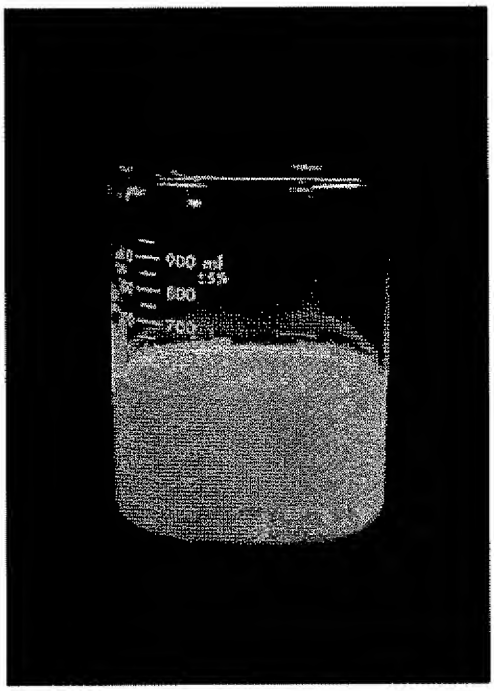
Dry Flowables

Dry flowables—or water dispersible granules, as they are sometimes called—are manufactured in the same way as wettable powders except that the powder

is aggregated into granular particles. They are diluted with water and applied in a spray exactly as if they were a wettable powder. Dry flowables, as would be expected, form a suspension in the spray tank; they have basically the same advantages and disadvantages as wettable powders, with several important exceptions. During the mixing and loading process, dry flowables pour more easily from the container and, because of their larger particle size, reduce inhalation hazard to the applicator.



Dry flowable before mixing

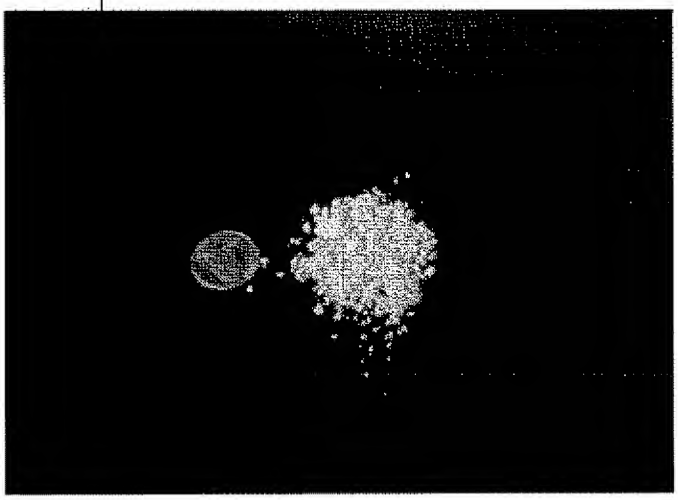


Dry flowable after mixing

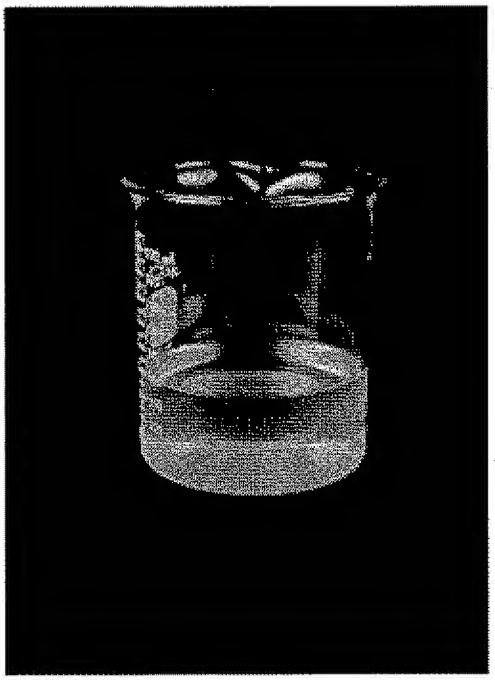
Note: The labels of some dry flowables do permit application of the product in the dry state.

Soluble Powders

Soluble powders, although not particularly common, are worth mentioning for purposes of contrast with the wettable powders and dry flowables. Their lack of availability is due to the fact that not many solid active ingredients are soluble in water. Those that do exist and are formulated in this fashion are mixed with water prior to spraying, dissolve in the spray tank, and form a true solution. Soluble powders provide most of the same benefits as wettable powders without the need for agitation once dissolved in the tank. They are also nonabrasive to application equipment. Soluble powders, like any finely divided particle, can present an inhalation hazard to applicators during mixing and loading.



Soluble powder before mixing



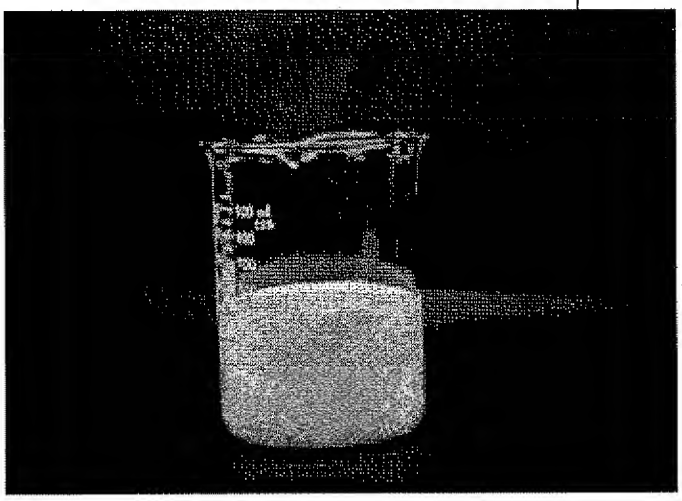
Soluble powder after mixing

Liquid Formulations

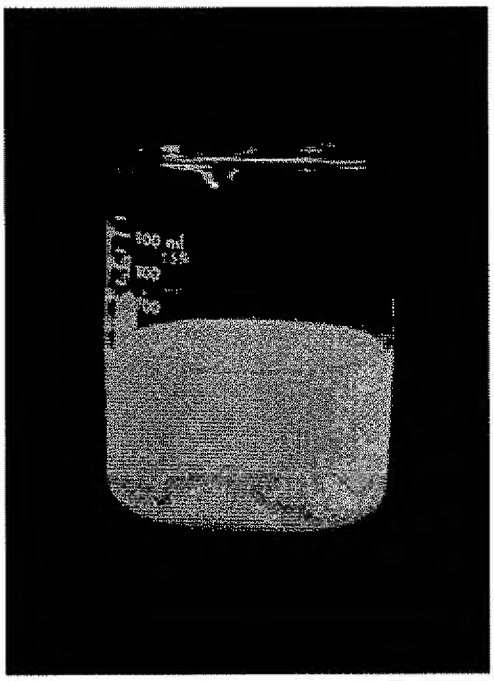
Descriptions of four, common liquid formulations that are mixed with a carrier follow. The carrier will generally be water, but in some instances labels may permit the use of crop oil, diesel fuel, kerosene, or some other light fuel oil as a carrier.

Liquid Flowables

The manufacture of liquid flowables (or flowables) mirrors that of wettable powders—with the additional step of mixing the powder, dispersing agents, wetting agents, etc., with water before packaging. The result is a suspension that is further diluted with water before use. The product is applied as a spray with all the advantages of a wettable powder. The benefit of this



Liquid flowable before mixing

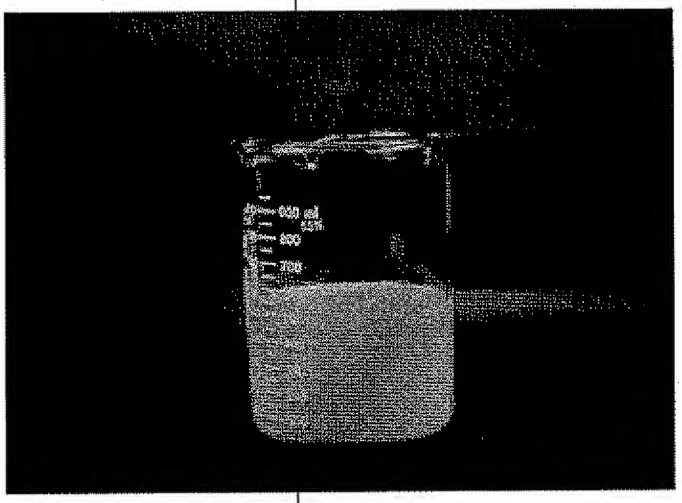


Liquid flowable after mixing

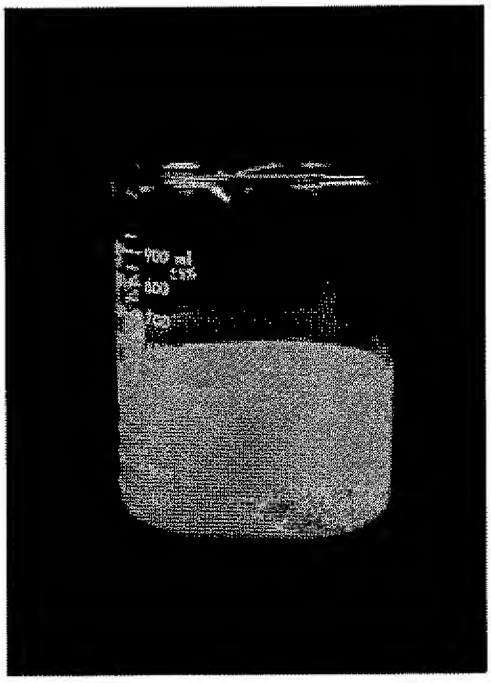
formulation is that there is no inhalation hazard to the applicator during mixing and loading since the powder already is suspended in water, permitting it to be poured. Liquid flowables form a suspension in the spray tank and have the same problems inherent in any suspension. However, they usually do not require agitation during application due to the extremely small size of the suspended particle but will settle if not tended to. One further problem noted with this formulation is the difficulty in removing all of the product from the container during mixing, loading, and container rinsing.

Microencapsulates

Microencapsulates consist of a solid or liquid inert (containing an active ingredient) surrounded by a plastic or starch coating. The resulting capsules can be aggregated to form dispersible granules (see dry flowables), or they can be suspended in water and the product sold as a liquid formulation. Encapsulation enhances applicator safety while providing timed release of the active ingredient. Liquid forms of microencapsulates are further diluted with water and applied as sprays. They form suspensions in the spray tank and have many of the same properties as liquid flowables.



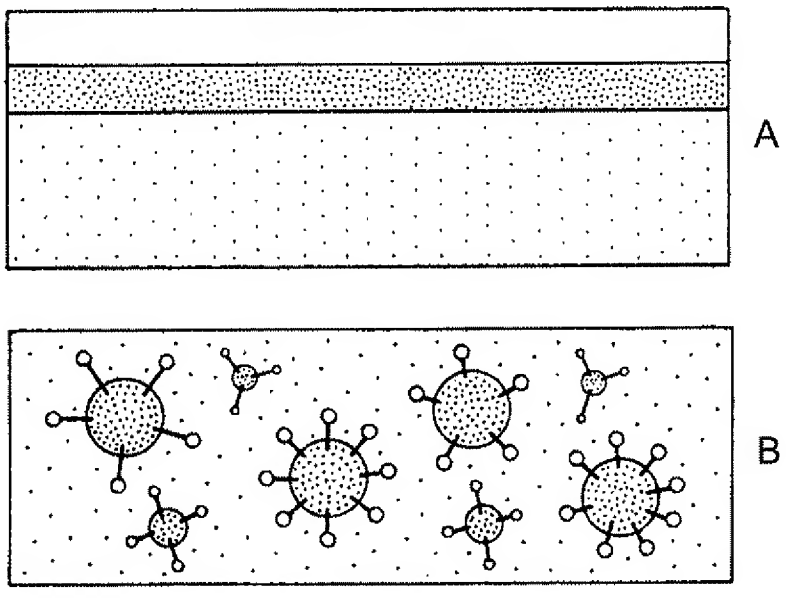
Microencapsulate before mixing



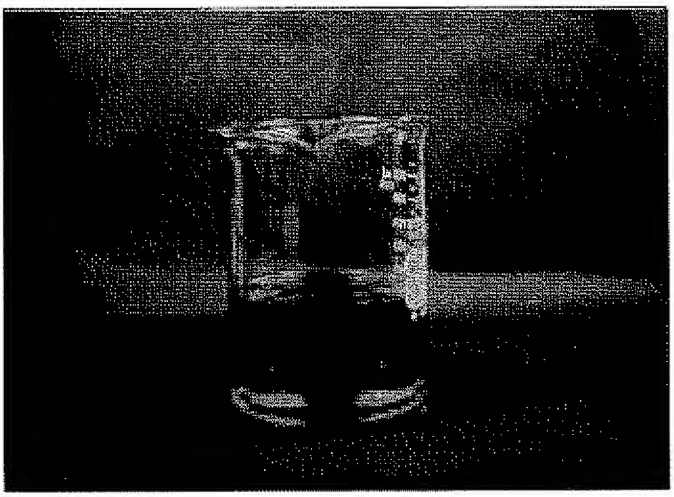
Microencapsulate after mixing

Emulsifiable Concentrates

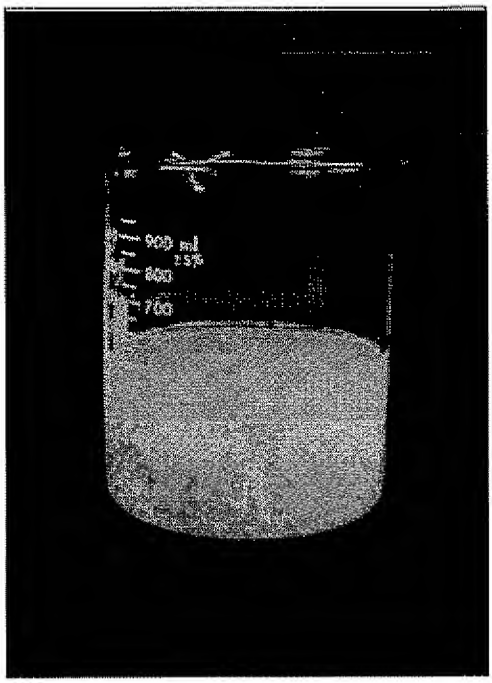
Emulsifiable concentrates consist of an oil-soluble active ingredient dissolved in an appropriate oil-based solvent to which is added an emulsifying agent. Emulsifiable concentrates are mixed with water and applied as a spray. As their name implies, they form an emulsion in the spray tank. The emulsifying agents are long-chain chemicals that orient themselves around the droplets of oil and bind the oil-water surfaces together to prevent the oil and water from separating. Emulsifiable concentrates allow oil-soluble active ingredients to be sprayed in water as a carrier. Some agitation is typically required to maintain dispersion of the oil droplets. They are not abrasive to application equipment, nor do they plug screens and strainers. Emulsifiable concentrates have several disadvantages. There is a dermal hazard associated with this formulation. Emulsifiable concentrates readily penetrate oily barriers like human skin. They usually have an odor problem, and can also burn foliage and cause the deterioration of rubber and plastic equipment parts.



(A) Water and oil without emulsifier.
(B) Emulsifiers link oil and water particles, enabling oil droplets to become suspended in water.



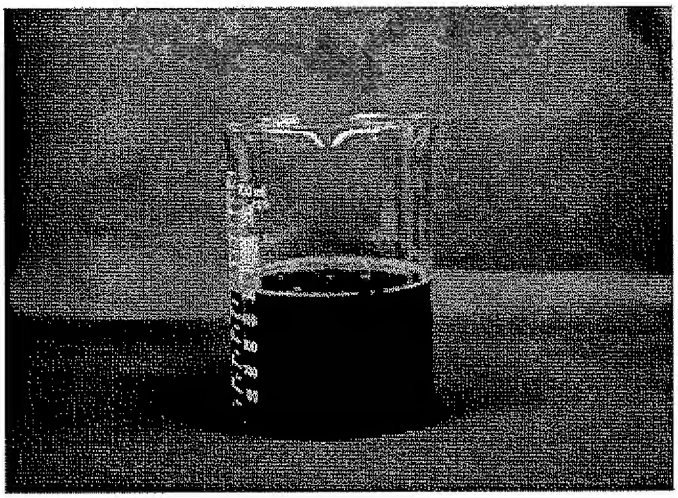
Emulsifiable concentrate before mixing



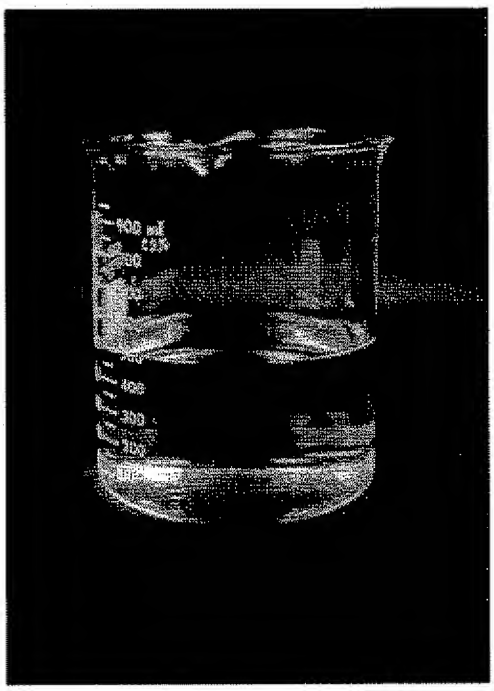
Emulsifiable concentrate after mixing

Solutions

Solutions (water-soluble concentrates) consist of water-soluble active ingredients dissolved in water for sale to the applicator for further dilution prior to field application. They will, obviously, form a true solution in the spray tank and require no agitation after they are thoroughly dissolved. Solutions are not abrasive to equipment and will not plug strainers and screens. Although not a particularly common formulation, several major herbicides with wide-scale use are formulated in this way. They include products containing paraquat, glyphosate and 2,4-D. Aside from lack of availability, solutions have few disadvantages; however, some that are produced as dissolved salts can be caustic to human skin.



Solution
before mixing

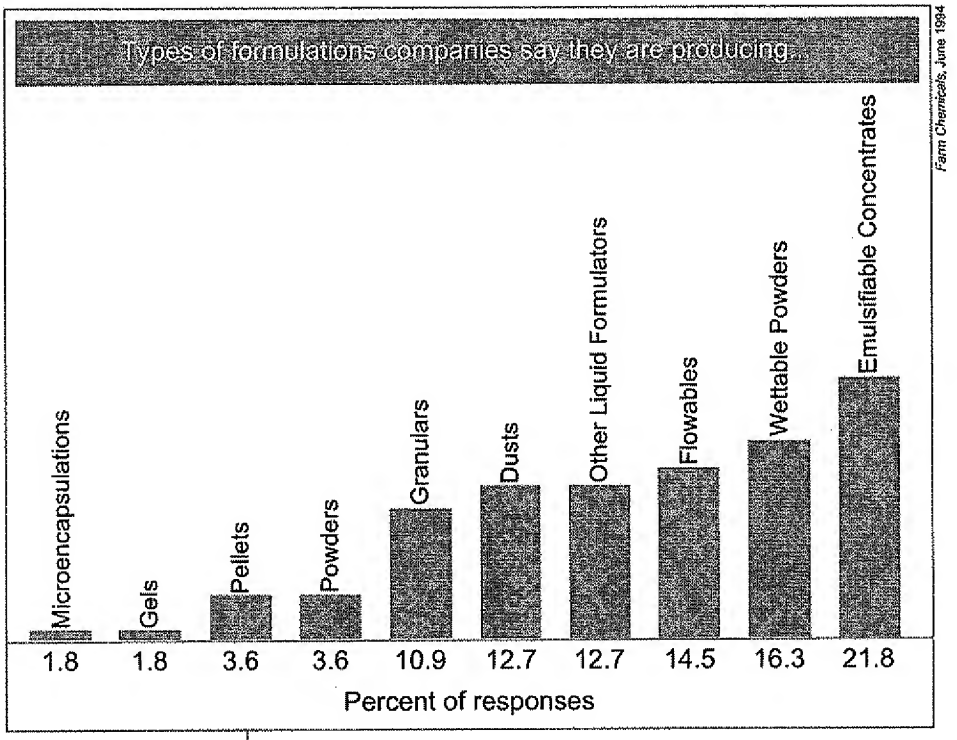


Solution
after mixing

Miscellaneous Liquid Formulations

Most liquid formulations are designed to be mixed with a carrier before application. However, some products are sold ready-to-use (RTU). This type of formulation generally will have a low concentration of active ingredient.

Low and ultra low volume concentrates used in specialty situations (e.g., space spraying and fogging) are frequently applied undiluted. Dermal hazards are a problem during mixing and loading of these products because of the high concentration of active ingredient. Low and ultra low volume concentrated formulations utilize special equipment to deliver the product in the form of very tiny droplets. Consequently, while they provide excellent coverage, drift potential and inhalation problems during application can be quite high.



Aerosols and Fumigants

These two formulations are frequently confused, yet they have very different properties and uses.

Aerosols really refer to a delivery system that moves the active ingredient to the target site in the form of a mist of very small particles: solids or liquid drops. The particles can be released under pressure or produced by fog or smoke generators. Aerosols are especially useful for indoor insect control, as coverage is thorough. It can be difficult to confine the aerosol to the target area, and there is always the danger of inhalation.

Fumigants deliver the active ingredient to the target site in the form of a *gas.* Some fumigants are solids that sublime (turn into a gas) in the presence of atmospheric moisture. Others are liquids under pressure that vaporize when the pressure is released. Fumigants can completely fill a space and many have tremendous penetrating power. They can be used to treat objects (e.g., furniture), structures, commodities, and even soil for pest insects and other vermin. Fumigants are among the most hazardous pesticide products to use due to their extreme inhalation danger.

FORMULATIONS AND LABEL INFORMATION

Product labels will often convey information about how the pesticide is formulated by a suffix to the brand or trade name. The table below lists many of these suffixes and their meanings. A suffix can also include a number that indicates the amount of active ingredient in the product. The number contained in the brand name suffix of a solid formulation such as a dust, granule, wettable powder, etc., describes the percent of active ingredient in that product on a percent by weight basis. For example, the brand name Sevin 50W® tells the purchaser that the product is formulated as a wettable powder (W) and that it is 50% active ingredient, *by weight*. The number included in the brand name suffix of a liquid formulation such as a liquid flowable (L) or an emulsifiable concentrate (EC) describes the amount of active ingredient in the product on the basis of *pounds per gallon*. The brand name Treflan 4EC® indicates that this product is formulated as an emulsifiable concentrate and that it contains *4 pounds* of active ingredient *per gallon* of product.

Exceptions to these rules of thumb common. Read the pesticide label carefully and consult the ingredient statement for a precise description of the active ingredient and its concentration.

Suffixes of Chemical Brand Names

Suffix	Meaning
Describe the formulation:	
AF	Aqueous Flowable
AS	Aqueous Suspension
D	Dust
DF	Dry Flowable
E	Emulsifiable Concentrate
EC	Emulsifiable Concentrate
ES	Emulsifiable Solution
F	Flowable
FL	Flowable
G	Granule
OL	Oil-Soluble Liquid
P	Pelleted
PS	Pelleted
S	Soluble Powder
SG	Sand Granules
SL	Slurry
ULV	Ultra-Low Volume Concentrate
W	Wettable Powder
WDG	Water-Dispersible Granules
WP	Wettable Powder

Suffix	Meaning
Describe how a pesticide is used:	
GS	For Treatment of Grass Seed
LSR	For Leaf Spot and Rust
PM	For Powdery Mildew
RP	For Range and Pasture
RTU	Ready-to-use
SD	For Use as a Side Dressing
TC	Termiticide Concentrate
TG	Turfgrass Fungicide
WL	To Be Used with Weed Killers
Describe characteristics of the formulation:	
BE	The Butyl Ester of 2,4-D
D	An Ester of 2,4-D
K	A Potassium Salt of the Active Ingredient
LO	Low Odor
LV	Low Volatility
MF	Modified Formulation
T	A Triazole
2X	Double Strength
Label for use in special locations:	
PNW	For Use in the Pacific Northwest
TVA	For Use in the Waterways of the Tennessee Valley Authority

The Safe and Effective Use of Pesticides, Pub. No. 3324, University of California

NOVEL APPROACHES TO PESTICIDE PACKAGING

Pesticide packaging is receiving tremendous attention in today's markets. The traditional manufacturing approach is to package liquid formulations into nonrefillable plastic containers or to place granular materials into multilayered paper bags. State prohibitions against the burning of pesticide containers and pressures on the applicator to eliminate the disposing of plastic and paper containers in landfills have placed a premium on finding alternative packaging to replace small, one-way containers. The interest in and research on container management has spurred the development and implementation of a new generation of pesticide packaging and recycling programs to help stem the flow of plastic containers entering solid waste landfills.

Solutions to the Nonrefillable Plastic Jug

Pesticide Container Collection Programs

Recycling programs aimed at reducing the number of plastic pesticide containers thrown away in landfills have been conducted among many state agencies and industries associated with agricultural production. Pesticide applicators bring properly rinsed pesticide containers to a collection site for inspection. Containers meeting inspection standards are passed through a chipping machine and reduced to recoverable plastic pellets. Pesticide container collection programs have been responsible for eliminating millions of pounds of plastic that otherwise would have been landfilled.

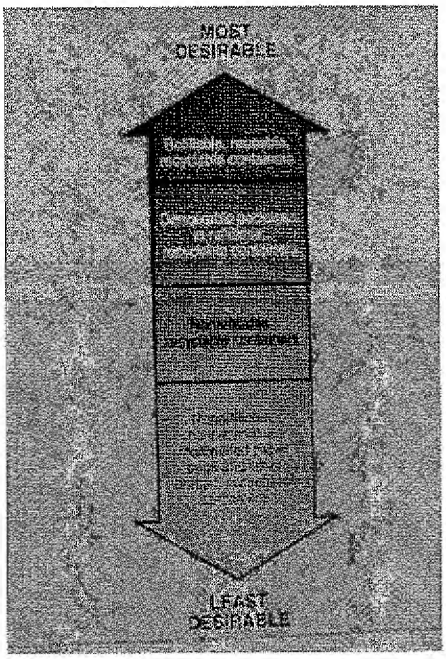
Returnable and Refillable Containers

Millions of 2 1/2-gallon plastic containers have been replaced with stainless steel tanks or plastic containers that hold larger volumes—5 - 250 gallons. These minibulk containers are transported to the site of application and, when emptied, are returned to the dealer or manufacturer for reprocessing and refilling. They are normally tamperproof, dedicated to a specific formulation, easily transported, and recyclable.

Water Soluble Packaging

Pesticide manufacturers are converting many products from a liquid formulation to a water-dispersible dry formulation, or incorporating them into a gel matrix. Both types of formulations are packaged in water-soluble pouches, with product and pouch enclosed in a moisture-proof bag or carton. The applicator tears off t

the outside protective cover and places the water-soluble bag into the spray tank. The bag dissolves and releases the dry or gel formulation into the water. The benefits of water-soluble packaging include limited exposure to the concentrated pesticides, elimination of the container rinsing process, enhanced emergency spill response, and reduction of the amount of waste placed in landfills.



Closed Granular Chemical Handling System

Granular formulations are packaged into multilayered paper bags. Recycling multilayered bags is difficult because the paper, foil, and, plastic layers prove difficult in separating and impossible in rinsing. One innovative approach has been to place the granular material into a closed pesticide handling system that mounts directly to the lid of the farmer's planter box. The container is returned to the supplier for refill. The solutions provided by the closed granular container systems are twofold: reduced applicator exposure, and the elimination of the multilayered paper bag.

SYNERGISTS

Synergists are chemicals that can boost the pesticidal activity of an active ingredient. The combination of a synergist with the active ingredient provides a degree of pest control greater than what would be expected from the simple additive effects from each compound. Synergists are used with a variety of pesticides including insecticides, nematicides, and fungicides. Synergists typically have little, if any, activity against the pest when used alone. However, EPA policy is to include synergists in the active ingredient statement on the product label.

A common example of a synergist is piperonyl butoxide. This chemical synergizes pyrethrin insecticides. It is believed to function by slowing down the insect pest's ability to metabolize (detoxify) pyrethrin resulting in fewer insects recovering from exposure to the insecticide.

ADJUVANTS

An adjuvant is *any* compound that facilitates the action of pesticides or modifies characteristics of pesticide formulations or spray solutions. The terminology for pesticide additives is confusing. It is often assumed that any material that lowers the surface tension of water (i.e., a surfactant) in the spray mixture or increases the wettability of the spray solution on surfaces is an adjuvant.

Adjuvants are used in pesticide spray solutions as

- wetting agents
- penetrants
- spreaders
- co-solvents
- stickers
- stabilizing agents

It is obvious that the term *adjuvant* encompasses a wider meaning than wetting agent or surfactant. There are many adjuvants that have little, if any, effect on pesticidal activity.

These types of adjuvants include

- anti-foam agents
- buffering agents
- compatibility agents
- liquid fertilizer/herbicide mixtures

Adjuvants are included in pesticide formulations as part of the total product which is sold by the manufacturer or as an additive to be mixed with pesticide products in the spray tank. Adjuvants can be classified according to their type of action.

There are three basic types of adjuvants used with pesticides:

- Activator adjuvants include surfactants, wetting agents, penetrants, and oils. Activator agents are the best known class of adjuvants because they are normally purchased separately by the user and added to the pesticidal solution in the spray tank.

- Spray modifier agents include stickers, film formers, spreaders, spreader/stickers, deposit builders, thickening agents, and foams.

- Utility modifiers include emulsifiers, dispersants, stabilizing agents, coupling agents, co-solvents, compatibility agents, and anti-foam agents.

Spray modifier agents and utility modifier agents are usually found as part of the pesticide formulation and thus are added to the pesticide product by the manufacturer.

SUMMARY

Becoming informed about the benefits and problems associated with the various pesticide formulations does not require a significant amount of memorization. Application of some basic principles of chemistry and consideration of formulation particle size can lead to some very accurate judgements about formulation properties. Several themes developed in this publication can be used to construct a planning or decision-making model.

The proper selection of a formulation is a critical step in any pest control process involving pesticides. It is an important management decision that has an impact on profitability, human safety, and environmental quality. An understanding of the properties of various formulations has as much significance to the applicator as it does to the supervisor. The applicator performs the duties of mixing and loading as well as application. Applicators come into close contact with both the concentrated and diluted product. A simple, personal interest in one's continued good health dictates the need to know the safety properties of the formulation being used. Furthermore, a concern for environmental quality reflected in a responsible application requires a familiarity with the attributes of a given formulation and the potential impact its use might have on the surroundings.

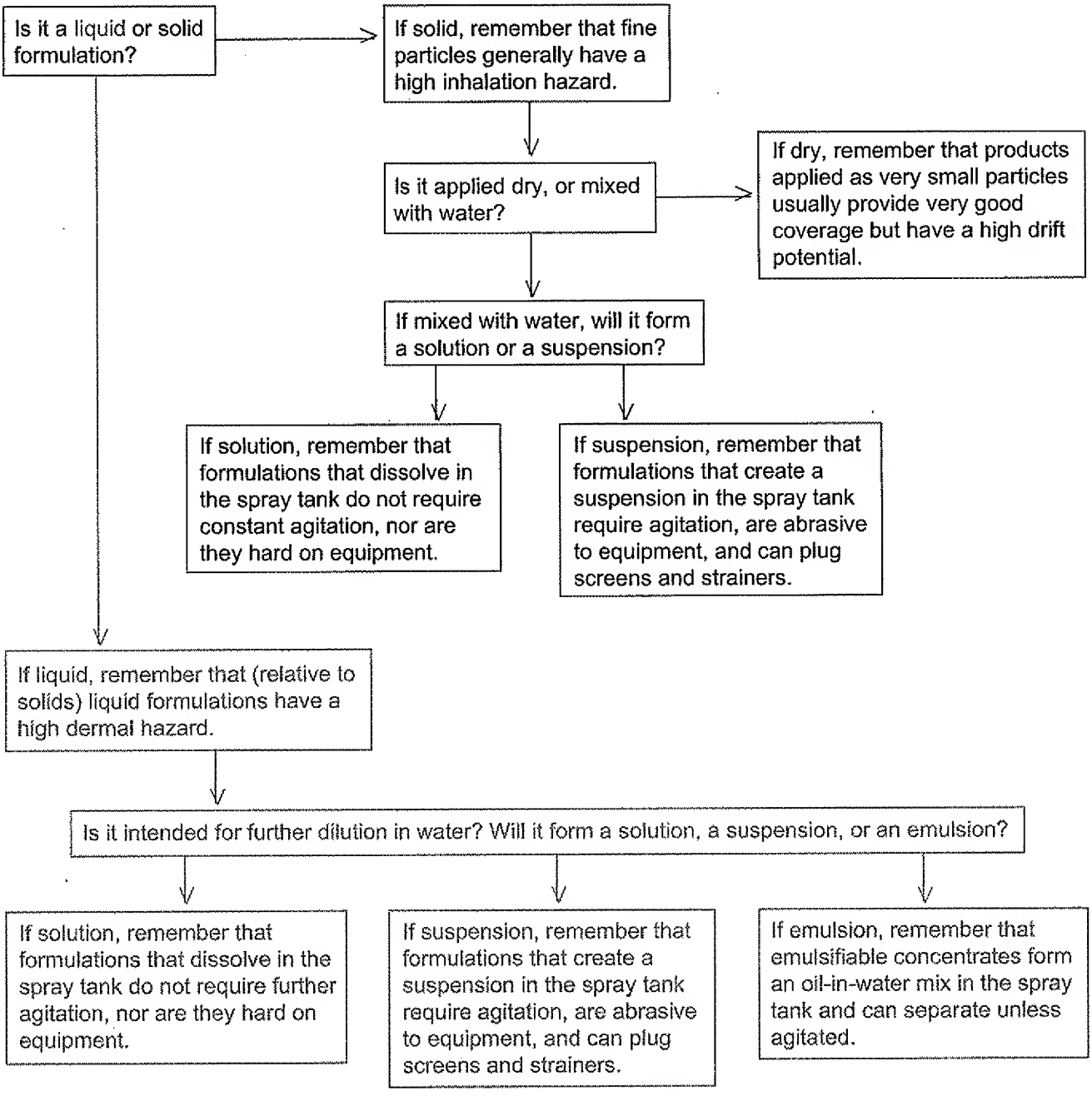
No endorsement of named products by the authors or Purdue University is intended, nor is criticism implied for products that are not mentioned. Always follow the directions on the label. Many different formulations and combinations of these materials are sold under various trade names, and the quantity of use will vary with the formulation obtained.

ACKNOWLEDGMENTS

The authors express their appreciation to the following individuals for their assistance in the preparation of this publication:

- Arlene Blessing for photographing the formulations and end-use dilutions depicted in the document.
- Mike Corbitt, Van Waters and Rogers, for his careful review of the manuscript and suggestions to incorporate the interests of the structural pest control industry.
- Jacque Sherman, CTX, Inc., for her very thorough review and contributions to the publication—especially in the area of synergists.

Ask yourself the following questions when selecting or using a pesticide formulation:



All liquid applications that produce tiny droplets can provide very good coverage but have high inhalation and drift hazards.

Reviewed 5/01

Copies of this publication can be obtained from the Purdue University Media Distribution Center, 301 South 2nd Street, Lafayette, IN 47905-1092.

EMULSIFIABLE CONCENTRATES - 3.2

Active Ingredients		Emulsifiers						Stabilizers and solvents			
		FF/4	FF/6	MS	V/497	V/87	---	---		Xylene	Shellsol ab
Endosulfan	35	1,8		3,2				EPO.	2	up to 100	
Ethion	50	3,5		1,5						up to 100	
Fenitrothion	50	2,3			5,7					up to 100	
Lindane	25	2,0		3,0				Cyclohexanone	25	up to 100	
Malathion	50	1,8			3,2					up to 100	
Malathion	57	2,5		2,5						up to 100	
Molinate	72,5	2,3					RE/70 : 2,7			up to 100	
Parathion	50	1,7	3,3							up to 100	
Parathion Methyl	50	3,5					RE/70 : 4,5			up to 100	
Pendimethalin	33,7	4,7				2,3				up to 100	
Phenmediphan	15,9						VB/55-N: 20	Isophorone	up		
								to 100			
Permethrin	5	2,7		3,3						up to 100	
Permethrin	25	3,0		3,0						up to 100	
Permethrin	5	3,3		2,7							up to 100
Permethrin	25	3,6		2,4							up to 100
Propanil	35						PR/500 : 16	Isophorone or			
								Cyclohexanone	30	up to 100	
Tetradifon	8	2,3		2,7						up to 100	
Thiobencarb	50	2,3		2,7						up to 100	
Toxaphene	75	3,0		2,0				EPO	2	up to 100	
Trifluralin	48	5,3		1,7						up to 100	

Legenda: EPO - Epoxidized soybean oil
MCB - Monochlorobenzene

For specific tradenames see pag. 65 Data Sheets 5.2

Above mentioned compositions are general examples; specific formulations are available on request.

FORMULATION SCIENCE

VOLUME I

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Making Useful Products Usable

RECENT TRENDS IN PESTICIDE FORMULATIONS

Kozo Tsuji

CONTENTS

ABSTRACT

This paper describes the objectives of pesticide formulations and the impact of newly emerging requirements of the pesticide industry. The importance of research work based on pesticide delivery system is pointed out. The problems of conventional formulations are discussed as well as

methods for their improvement giving rise to new formulations types. New and promising formulations such as water-based formulations, water dispersible granules, water soluble packages, controlled release formulations such as microcapsules and polymeric pesticides, biopesticide formulations and other functional formulations are reviewed; their advantages and future trends are also discussed.

I. INTRODUCTION

A. PURPOSES OF PESTICIDE FORMULATIONS

Pesticides are usually effective at several grams to hundreds of a grams of active ingredient per 10 ares (1000^2 meters). However, it is very difficult to apply such a small amount uniformly to a broad field. Therefore, pesticide technical materials are diluted with suitable solid or liquid diluents in order to spray or apply easily. This is "Pesticide Formulation". In this case, biological efficacy, storage stability, safety, easy handling, and cost should be taken into consideration to commercialize pesticide formulations.

The purposes of such pesticide formulations are summarized as follows:

- To make handling and application of the pesticides easy.
- To maximize biological efficacy.
- To improve defects in the pesticide.
- To make pesticides safer for workers and users.
- To reduce harmful effects and impact on the nontarget organisms and the environment.
- To improve work efficiency that results in labor savings.
- To give various functions to pesticides in order to broaden their spectrum of activity.

B. RECENT REQUIREMENTS OF PESTICIDE INDUSTRY

A recent trend is the more stringent regulatory requirements on the pesticide industry, especially with regard to toxicity. Pesticides are being required to satisfy the following conditions.[81]

- Higher safety: A pesticide should be safe for workers and have no harmful effect or impact on nontarget organisms or the environment.
- High efficacy: Pesticides should have good initial and residual efficacy at lower dosage.
- Lowest possible price: Manufacturing cost should be low and cost performance should be good.
- Less labor intensive: The application should be easy and application efficiency should be high.

It is not easy for candidate compounds by themselves to satisfy all these requirements. It has thus become very difficult to develop new pesticides; the cost and time for the development of a new pesticide has increased

significantly. Therefore, it becomes very important to improve formulation and application technology in order to satisfy the above requirements for new and existing active ingredients. To this end, formulation research has become very important; meeting the last four items in the above list has become essential.

II. PESTICIDE DELIVERY SYSTEM

In order to meet recent requirements of pesticide industry, the concept of "Pesticide Delivery System" (PDS) is very important.[30,78,81] PDS can be defined as a technique or a method in which active ingredients are made available to a specified target at a concentration and duration designed to accomplish an intended effect, i.e., obtain the fullest biological efficacy while minimizing various harmful effects. The concept of PDS is very similar to that of Drug Delivery System (DDS). However, as compared to DDS, PDS has the following difficulties that have to be addressed.

- PDS is an open system, while DDS is a closed system.
- PDS has variable conditions of natural circumstances, while DDS has constant conditions such as temperature.
- PDS has no natural delivery vehicle to the targets such as insects, fungi and weeds, while in the case of DDS the blood delivers the drug to the target organs.
- In the case of PDS, cheaper materials and technologies can be used – as pesticide users are much more cost-conscious than consumers of pharmaceutical drugs.

Therefore, PDS are not as easily formulated as are DDS. However, research work about formulation and application technologies based on this concept should be continuously carried out.

III. IMPROVEMENT OF FORMULATIONS AND APPLICATION TECHNOLOGIES.

Various improvements of formulations and application technologies have been made according to the recent demand of the pesticide industry. Changes in formulation types have also proceeded and various new types of formulations and application methods have been developed.

Table 1 shows some of the problems of conventional formulations, the reasons behind these problems, and methods for reducing them in new pesticide formulations being developed.[76,78,79]

Emulsifiable concentrates (EC) have problems of toxicity, phytotoxicity and flammability that are caused by organic solvents and synthetic surface-active agents used in EC.

One of the improvement methods is making use of water, the safest liquid, instead of organic solvents in emulsions and microemulsions. The

other method is solidifying of EC formulations, which results in emulsifiable granules or powders). Another method is making use of safer organic solvents and emulsifiers.

Table 1
Development of New Pesticide Formulations

Formulation	Problems	Reasons	Improvement methods	New formulations
Emulsifiable Concentrate	Toxicity; phytotoxicity; flammable	Organic solvent, suface active agents	Use water; solidify; change solvents or emulsifiers	Concentrated emulsions (EW, CE) Microemulsions (ME) Suspoemulsions (SE) Emulsifiable granule or powder
Wettable Powder	Dusty	Fine powder	Water dispersion, granulate, package in water soluble bags	Suspension concentrate (SC, Flowable) Water dispersible granule (WDG) Water soluble packages
Dust	Drift; dusty	Fine powder	Granulate: remove fine particles	DL dust Fine granule F
Flowable	Deterioration of physical properties	Dispersion in liquid	Remove liquid Improve recipe	Dry flowable Improved formulation
Granule	Weight	3-kg/10 are	Higher concentration	1 Kg granules

Wettable powders (WP) have a problem of dustiness, both at the time of dilution and after drying of the sprayed liquid, that is caused by fine mineral powder used in the WP as diluents. One of the improvement methods is dispersing WP's in water to make a flowable formulations. The other method is granulating WP to result in water dispersible granules (WG). Another method is packaging the WP in water-soluble packages.

Dust has a problem of drift, which is caused by fine mineral powder used as carriers. One method of improvement is by removing particles less than 10 microns resulting in a DL dust (driftless dust having an average particle size >20 microns). Another method of improvement is granulating the formulation into fine granules (F) having a particle size of 63-212 microns. Both the DL dust and the fine granule F have been developed in Japan.

Flowable formulations have a problem of deterioration of physical properties, that is, sedimentation. One improvement method is to remove the liquid resulting in dry flowable, water-dispersible powders.

Granule formulations have a problem of weight, considering application rates of 3-kg per 10-ares that is common in Japan. The method of improvement is to increase the active ingredient concentration in the formulation. A new, higher dose 1-kg granule formulation which will treat 10-ares, has been introduced in Japan.

Table 2 shows general recent requirements in the pesticide industry, methods of improvement, and new types of formulations.

Controlled release formulations such as microcapsules are developed for improved safety, labor saving, and improved biological efficacy.

For labor saving, there have been developed application methods of pesticides from levees and water inlets of paddy fields, application at the same time of transplantation, application to the nursery box, seed treatments and application of pesticides with fertilizers. Corresponding to these application methods, various new types of formulations have been developed such as jumbo herbicides, water surface spreading formulations, and fertilizers containing pesticides.

Biopesticides are also developed for improved safety and improved biological efficacy.

From these arguments, it is clear that improvements can be summarized as follows:

- Using water instead of organic solvents resulting in water-based formulations.
- Granulation or water-soluble packaging of dusty formulations.
- Development of controlled release formulations such as microcapsules, laminates, granules, and polymeric pesticides.
- Development of various functional formulations such as jumbo formulations, water surface spreading formulations, and fertilizers containing pesticides.
- Using various kinds of biopesticides.

Table 2
Recent Requirements in the Pesticide Industry, Methods of Improvement, and New Types of Formulations

Recent Requirements	Methods of Improvement	New Types of Formulations
	Controlled release	**Controlled Release Formulation** (microcapsule, laminate, granule)
Improved safety Labor-saving Improved biological efficacy	Exposure reduction; Application from levee; Application from water inlet of paddy field; Application of pesticides to nursery box; Application of pesticides at the same time of transplantation; Seed treatment	Water soluble package Jumbo herbicide
	Application of pesticides with fertilizers	Fertilizer containing pesticide
	Making use of biopesticide	Biopesticide formulation
	Targeting	Surface spreading formulation

IV. NEW AND PROMISING FORMULATIONS

A. WATER-BASED FORMULATIONS[76-78]

Water-based formulations are obtained by emulsifying or suspending pesticide technical materials in water. Water is the safest liquid. Therefore, water-based formulations have various advantages from a safety point of view. On the other hand, they have also some kinds of disadvantages. For example, pesticides that are unstable in water can not generally be formulated into water-based formulations. However, various kinds of technologies have been developed to stabilize the pesticides that are unstable in water. Each water-based formulation will be discussed in more detail.

1. Emulsion, Oil in Water (EW)[21,30,45,58,62]

This formulation is obtained by emulsifying or dispersing water-insoluble pesticides in the liquid state in water by means of proper emulsifiers. The pesticides, which are liquid at room temperature, can be dispersed as they are in water. Solid pesticides are dissolved at first in water-insoluble organic solvents, and then dispersed in water. In this case, it is better that water solubility is lower than 1000 ppm. This formulation includes active ingredients, emulsifiers, thickening agents, antifreeze, preservatives, defoamers, (organic solvents), and water. As emulsifiers, synthetic emulsifiers are commonly used such as the mixture (HLB >14) of polyoxyethylene (40 mole) castor oil ether and polyoxyalkyleneglycol ether, and water soluble polymers such as polyvinyl alcohol and gum arabic, which act as protective colloids are also used. As thickening agents, acrylic polymers, cellulose derivatives, and xanthan gum are frequently used, as these materials show thixotropic properties. Fine mineral powders such as bentonite, hydrated silicon dioxide are also applied.

The advantages of this formulation are as follows:

- Reduced toxicity and irritation.
- No dust problems.
- Nonflammable.
- Better efficacy than WP due to smaller particle size.
- Reduced phytotoxicity.
- Nonstaining.
- Reduced smell.
- Plastic bottles can be used.

The disadvantage is that an emulsion is thermodynamically unstable dispersion. Therefore it tends to lose its uniformity after keeping for long time at room temperature through coalescence, coagulation, creaming, or settling to result in phase separation. The emulsion is also very sensitive to temperature. Therefore, stability of the emulsion may be lost by change of temperature. Dissolving them in organic solvents can often stabilize

emulsions of pesticides that are unstable in water.

2. Suspension Concentrate (SC, flowable)[11,30,55,62,69]

This formulation is obtained by suspending solid water-insoluble pesticides in water. The purpose of this formulation is to formulate pesticides insoluble in both water and organic solvents, into flowable liquid formulation. These formulations contain active ingredients, dispersing agents, wetting agents, thickener, anti-freeze, preservatives, defoamer, specific gravity adjuster and water. Pesticide technical materials should satisfy the following conditions.

- Melting point is higher than 60°C.
- Water solubility is less than 100 ppm.
- They should not be easily hydrolyzed.
- They can be milled to small particles and Ostwald ripening does not take place.

Dispersing agents act as dispersion stabilizers. There are two stabilization mechanisms, static electric repulsion force and steric stabilization.[11,18,27,61] In order to stabilize by static electric repulsion force, anionic Surfactants such as polyoxyethylene phosphate and polyoxyethylene sulfates are widely used. These surfactants adsorb to the dispersed particles to give a negative electric charge, which stabilizes the dispersion by the repulsion force between negative charges. Polymers and high molecular weight nonionic surfactants form thicker adsorbed layers on the dispersed particles. For steric stabilization, water-soluble polymers such as lignosulphonate, polyvinylalcohol and alkylnaphthalene formalin condensates are often used. As wetting agents, which make pesticide technical materials wet in water, polyoxyethylene alkylphenylether and polyoxyethylene sorbitan ester are often used. Dispersing agents may act also as wetting agents. As thickeners, the same materials as described in "emulsion" can be used. Colloidal microcrystalline cellulose is also used for a thickener.[29] Inorganic electrolytes such as sodium chloride and calcium chloride act as specific gravity adjusters to reduce differences between specific gravities of liquid layers and dispersed particles. It is also reported that polyethyleneglycol enhances the stability of concentrated suspension.[40]

The advantages of this formulation are the same as those of "Emulsion".

The disadvantages are as follows:

- Hydrolyzable pesticide technical materials can not be formulated to this formulation.
- Sometimes a hard cake is formed.
- High concentration formulation is impossible.
- Wet grinding process is expensive.

Stable suspension formulations of hydrolytically unstable sulfonylurea compounds were developed by the regulation of suspension pH and

complexation.[28]

This formulation is usually sprayed after dilution with water. Recently there have been developed flowable herbicides which have good diffusion properties in water and can be applied without dilution by hands from levees of paddy fields[70-72] smaller than 0.3 ha. In this case, proper surfactants are chosen for active ingredients to diffuse and spread smoothly in water. The concentration of active ingredients reaches an even level within 1-day in paddy water and within 3-days on the soil surface. This application method of flowable proved to reduce labor intensity in applications by 30% in comparison with conventional granular herbicides.

In order not to stick to rice and to reduce phytotoxicity, surface tension is adjusted to be 36-65 dyne/cm at 25°C by selecting appropriate surfactants.[70,71]

Another application method has been developed where the flowable herbicides are added to the irrigation water inlets.

3. Suspoemulsion (SE)[30,42,62,89]

This formulation is a combination of emulsion and suspension. Both solid and liquid technical materials are dispersed in water. Usually, solid technical materials are formulated into SC and liquid technical materials are formulated into EW; when they are sprayed at the same time, they should be tank-mixed before application. It is a great advantage of suspoemulsions that water-insoluble solids and liquid technical materials can both be dispersed/emulsified with water being the continuous phase. The advantages of this formulation are the same as those of EW and SC. By using suspoemulsions, not only are the number of applications reduced resulting in savings in time and money, but formulation costs can also be reduced. This formulation is very promising because of its safety and application advantages, but few such formulations have been developed due to the difficulty to develop stable formulations, as mentioned below.

In suspoemulsions, generally two kinds of surfactants are necessary, emulsifier to emulsify oily liquid technical materials and dispersant to disperse solid technical materials. They should be compatible in one formulation. A proper surface active agent may act as both an emulsifier and a dispersant. When adsorption characteristics to solid and emulsion particles are different, stable emulsion or dispersion can not be obtained. Therefore, selection of appropriate surfactants is significantly important but considerably difficult. At present, they are selected by the method of trial and error for each formulation. However, an easy method for the preparation of a suspoemulsion using latexes as emulsion stabilizers was also been reported.[43] Alkylglucoside surfactants have been successfully utilized in both phases of a suspoemulsion.[15]

Microemulsion (ME) [30,45]

Microemulsion is a transparent or semitransparent, one liquid phase, and thermodynamically stable emulsion system. Particle sizes of microemulsions are about 0.01-0.1 microns. Therefore, neither creaming nor settling takes place during storage. This formulation has advantages similar to emulsions, but the following additional advantages are realized:

- Emulsion is quite stable for a long time.
- Emulsion particle size is smaller than that of EC, and biological efficacy may be superior.
- It has a clean image and the value of commercial goods is high.

There are, however, some drawbacks as follows:

- High concentration formulation can not be made.
- It is transparent even after dilution. Therefore, it is difficult to know whether it is diluted or not.

This formulation contains active ingredients, emulsifiers, cosurfactants, and water. When active ingredients are solid, water immiscible organic solvents such as aromatic hydrocarbons are used to dissolve them. The amount of emulsifiers is larger than that in emulsion. For example, about 20% emulsifiers are necessary in order to make microemulsion containing 10% of active ingredients. Combinations of strong hydrophilic (HLB >13) and high molecular weight nonionic surfactants and hydrophobic anionic surfactants are the preferred emulsifiers. For example, polyoxyethylene (15-30 mole), styrylphenol ether, polyoxyethylene phenylphenol ether, and calcium dodecylbenzene sulphonate are used for microemulsions of pyrethroid and organophosphorus insecticides.[30,87] Tristyrylphenol-based surfactants are also used for microemulsion of pyrethroids.[10] Stable microemulsion was obtained by using mixed surfactants, one being a higher N-alkylpyrrolidone, which functioned as interfacial solvents.[46] As cosurfactants, nonionic surfactant with low HLB or C_4 to C_{10} alcohols[57] are used in order to lower the HLB of the formulation and to reduce surface tension between water and oil. As solvents, fatty acid methyl ester containing carbon chain length of 8-12 provide maximum solubility and emulsification characteristics.[64]

Multiple Emulsion[1]

This formulation is an emulsion of an emulsion. In the w/o/w multiple emulsion, active ingredients within the inner water phase can not diffuse freely into the external continuous water phase. Therefore, it is possible to put incompatible active ingredients in other compartments within a single formulation. The multiple emulsions reduce toxicity significantly. This formulation type is just starting to be applied to pesticide formulations, and improvement of formulation stability is essential.

B. WATER DISPERSIBLE GRANULE (WG, DRY FLOWABLE)[12,23,30,62,76-79,85]

Water dispersible granules were developed to prevent dustiness of wettable powders at the time of dilution, and this formulation disintegrates and disperses readily in water after application.

The advantages of this formulation are as follows:

- Dust free and safe for workers.
- High density and compact packaging.
- Constant apparent density and measurable by volume.
- Good flowability and superior handling.
- Possibility of high concentration formulation.
- Packageable in paper bags and various containers.
- Little residue in the container and the used containers are easily disposed of.

Water dispersible granule can be formulated by various methods. Characteristics of each method and physicochemical properties of WG formulated by each method are summarized in Table 3. It is clear that the physicochemical properties of WG depend on formulation methods. Formulation recipes should be varied according to the formulation methods.

Water dispersible granules generally contain active ingredients, wetting agents, dispersants, fillers, binders, disintegrants, antifoams, and adjuvants. The kind of dispersants in the formulation is the most important.

The development of water dispersible granules of liquid and low melting technical materials was initially difficult, but recent advances in technology have simplified this problem. In this case, the most important factor in the formulation is the carrier. It was found that the low melting technical requires precipitated silica and that the liquid technical requires calcium silicate.[44]

Commercial water dispersible granules are formulated mainly by either a spray drying method, pan granulation method, high speed mixing method, or extrusion method. Recently, the extrusion method has become more popular.

C. WATER-SOLUBLE PACKAGES[20,24,68]

Water-soluble packaging of pesticides has various advantages as follows:

- Reduction of worker exposure at the time of dilution of a WP.
- Safe and easy handling.
- Unit dose convenience.
- Uncontaminated packaging waste.

Water-soluble packaging has been carried out for about 20 yr, mainly because of the first two advantages mentioned above. This has become very important from the viewpoint of package disposal. When water-soluble bags are used for pesticides, the outer layer has to protect the inner bag from

moisture and also be uncontaminated with the pesticide. This is a big advantage for disposal of the packaging materials.

Polyvinylalcohol (PVA) is the most used water-soluble film. The physicochemical properties of PVA have been improved significantly, including water solubility, physical strength, processability, and stability. More products are being packaged in water-soluble bags due to the above mentioned advantages. Initially solid formulations were packaged in water-soluble bags, and later liquid formulations such as EC were also packaged in water-soluble bags. In this case leaking through pinholes took place. Therefore recently, high viscous gel formulations are packaged in water-soluble bags instead of EC.

In Japan, herbicide granules packaged by water-soluble film have been developed for labor - saving application. This formulation is one kind of *jumbo herbicides* as described later.[32,48] This packaged formulation, which is discussed in more detail below, is thrown by hand from levees into a paddy field. Recently the similar application method of granules packaged by water-soluble film has been developed for insecticides and fungicides. In these cases, most of the granules are spread on water surface to get better biological efficacy.

Water-soluble bottles (50 ml) made of PVA are also used for an oil formulation for rice pest control which spreads over the entire water surface of the paddy field in a few minutes. Six to ten bottles are thrown by hand from the levees into 10-are paddy field.

Table 3
Granulation Methods of WG and Their Characteristics

Granulation Method	Manufacturing conditions			Physicochemical properties of WG			
	Milling	Moisture Content to be dried (%)	Drying temperature (°C)	Shape	Particle size (mm)	Disintegrability in water	Manufacturing Cost
Spray drying	Wet	40-50	>100	Spherical	0.1-0.5	Excellent	Expensive
Fluidized bed drying	Wet	40-50	50-80	Nearly spherical	0.1-1.0	Excellent	Expensive
Freeze drying	Wet	40-50	<0	Irregular	0.5-3.0	Good	Moderately expensive
Pan granulation	Dry	10-15	50-80	Nearly spherical	0.2-3.0	Good	Cheap
Extrusion	Dry	10-15	50-80	Cylindrical	0.7-1.0	Poor	Cheap
High speed mixing	Dry	10-15	50-80	Irregular	0.1-2.0	Good	Moderately expensive
Fluidized bed	Dry	20-30	50-80	Nearly spherical	0.1-1.0	Good	Moderately expensive
Compression	Dry	0	—	Irregular	0.5-3.0	Poor	Cheap

D. CONTROLLED RELEASE FORMULATIONS

1. Microcapsules (CS)[78,84]

Microcapsules (MC) are small particles (1-1000 microns) composed of a core material and an outer wall. The wall isolates the core material from the environment and protects it from environmental degradation and interaction with other materials. The core materials are designed to be released in a controlled fashion as required. Some review articles are available in the literature.[62,76-86]

Microencapsulation of pesticides is mainly carried out by interfacial polycondensation, *in situ* polymerization and coacervation. Among these methods, interfacial polycondensation is the most useful method for industrial production. Controlling the amount of monomers and process conditions can control particle size and wall thickness relatively easily.

Various polymers used for wall materials of pesticide microcapsules should satisfy the following conditions:

- The polymers have appropriate molecular weight, glass transition temperature, and molecular structure in order to achieve proper release rate.
- The polymers do not react with the pesticides.
- The polymer and its degradation products must not cause any environmental pollution.
- The polymer should be generally stable during storage and usage, and easily manufactured and fabricated into the desired product at acceptable costs.
- For agricultural application, polymers should be biodegradable to avoid environmental pollution.

The general advantages of pesticide microcapsules are as follows:

- Controlled or slow release of core a.i. to result in improvement of residual activity.
- Longer application interval resulting in laborsaving.
- Reduction of application dosage.
- Stabilization of core a.i. against environmental degradation (light, air, humidity, microorganism, etc.).
- Reduction of mammalian toxicity.
- Reduction of human mucous-membrane irritation.
- Reduction of phytotoxicity.
- Reduction of fish toxicity.
- Reduction of evaporation and leaching.
- Reduction of environmental pollution.
- Reduction of reactivity of two insecticides.
- Masking of odor.
- Solidification of liquid pesticides.
- Reduction of drift.

- Increase in the number of target organisms.
- Consistent activity irrespective of application surfaces.
- Easier handling.

An MC does not necessarily have all of the above advantages. Therefore, the proper design of the MC is very important in order to obtain the desired characteristics according to the purpose of the application.

In order to be biologically effective the pesticide must be released from the MC. There are two mechanisms for release.

- Diffusion through the MC wall.
- Destruction of the MC wall by either physical destruction, i.e. mechanical power; or by chemical destruction, i.e. hydrolysis, biodegradation, thermal degradation, etc.

The release behavior described above is controlled by factors such as particle size, wall thickness, type of wall materials, wall structure (porosity, degree of polymerization, crosslink density, additives, etc.), type of core materials (chemical structure, physical state, presence or absence of solvents) and amount or concentration of core materials. Release behavior is determined by interaction of these factors, and optimization is very important for each usage.

In order to get better performance of the MC's for biological efficacy and safer behavior both to workers and environment, time-dependent or site-specific release is desirable. For this purpose, it is essential to develop various functional MC's such as stimuli-responsive MC's that are specific to target organisms. For example, physical pressure-, temperature-, pH-, light-, enzyme- and ion- responsive MC's are desired. These technologies are developing in other application fields.

Examples of commercial pesticide MC's available in Japan are summarized in Table 4. Note that there are more than 60 MC's currently available on the world market. Some of them have been developed very recently. Therefore research and development of microencapsulated pesticides has grown significantly in recent years. This growth has to do with the fact that a lot of advantages mentioned before can meet the current demands of the pesticide industry, that is, safer formulations and application methods which are more labor-saving and environment-friendly. Some examples of functional MC's are explained.

Fenitrothion MC's for cockroach control were developed.[33,53,54,75,80-83,86] The wall material is polyurethane. They were prepared by interfacial polymerization.

These MC's at the rate of 125 mg of a.i./m^2 caused 100% mortality to the German cockroaches even 8-wk after treatment.[33,86] Such a long-lasting residual activity is probably caused by the trampling mechanism, that is, the cockroaches broke the MC's when they contacted the MC's. Breaking of the MC's was confirmed by the microscopic observation of the MC's before and after contact of the cockroaches. Distribution of fenitrothion before and after

cockroaches crawled on the MC-treated petri dish is shown in Fig. 1.[75,86] The amount of fenitrothion outside the MC's was almost negligible before contact. After cockroaches contacted the MC's, however, the amount of fenestration outside the MC's increased significantly. It was also clear that fenitrothion adhering to the body of the cockroaches was 10 times more than that in the viscera.

If trampling is the mode of action, biological efficacy is dependent on the strength of the MC's. It was found that the trampled percentage of MC by the contact of cockroaches can be controlled by D/T as shown in Fig. 2, where D is a mass median diameter and T is a wall thickness.[53,86] D/T is known to be a parameter of MC strength. When the value of D/T is set properly, both initial and residual efficacy were good.

Table 4
Examples of Commercial Pesticide Microcapsules Available in Japan.

Trade name*	Active ingredient	Wall material	Company
Aniverse MC	halfenprox		Mitsui Toatsu Chemical
Baktop	fenobcarb	Polyurethane	Sumitomo Chemical
Diazinon MC	diazinon	polyamide/polyurea	Nippon Kayaku
Diazinon SL Sol	diazinon	polyurea	Nippon Kayaku
Ember MC	permethrin	polyurethane	Sumitomo Chemical
Gokilaht MC	cyphenothrin		Sumitomo Chemical
Guardjet wp (Cell Cap)	*Bacillus thuringiensis* fixed ssp. san diego toxin	*Pseudomonas Fluorescens*	Kubota (Mycogen Corp.)
Kareit MC	fenitrothion	Polyurethane	Sumitomo Chemical
Kayatack MC	chlorpyrifos	Polyurea	Nippon Kayaku
Lentrek 20MC	chlorpyrifos	melamine urea resin	Dow Elanco Nippon
Lumbert MC	fenitrothion	polyurethane	Sumitomo Chemical
Mocap 3MC	ethoprophos	melamine resin	Rhone-Poulenc Yuka Agro
Naramycin D80	cycloheximide	melamine resin	Tanabe Pharm,
Deet MC	DEET	melamine resin	SDS Biotech Toppan Moor
Sumi Cue-lure microcapsule sol	fenitrothion +Cue-lure	gelatin/gum arabic	Sankei Chemical, Toa Gosei
Sumipine MC	fenitrothion		Sumitomo Chemical
Sumithion MC	fenitrothion		Sumitomo Chemical
Sumithion MC for cockroach control	fenitrothion		Sumitomo Chemical

* These are trade names of each company.

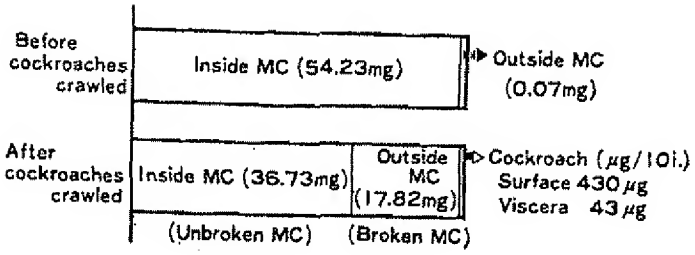

Figure 1. Distribution of fenitrothion (inside and outside the microcapsules) before and after cockroaches crawled on the microcapsule-treated petri dish. (From Tsuda, S., Ohtsubo, T., Kawada, H., Manabe, Y., Kishibuchi, H., Shinjo, G. and Tsuji, K., *J. Pesticide Sci.*, 12, 23, 1987. with permission.)

If the MC's are too weak, where D/T is large, initial efficacy is good but residual efficacy is poor. On the other hand, when the MC's are too strong and no breaking takes place, neither initial nor residual efficacy is good. When the cockroaches trample the MC's, the a.i. is released and kills the target insects. These MC's are activated only when the cockroaches make contact with them. This mechanism is similar to that of land mines. Therefore, these MC's could be called land mine-type MC's.

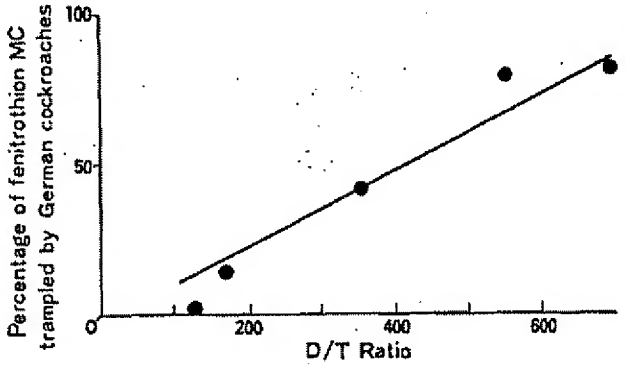

Figure 2. Relationship between the D/T ratio and the percentage of fenitrothion microcapsules (MC) trampled by German cockroaches on a petri dish after 2 hours. (From Ohtsubo, T., Tsuda, S., Kawada, H., Manabe, Y., Kishibuchi, N., Shinjo, G. and Tsuji, K., *J. Pesticide Sci.*, 12, 43, 1987. with permission.)

Discussion of physical strength of the MC's was also reported. The relationship between D/T and P_{50}, pressure at which 50% of the MC's were

broken, was explained by modifying the theory of destruction of an empty sphere with thin wall.[54]

A cyphenothrin microcapsule was also developed for cockroach control.[34] The mode of action is the destruction of MC's by cockroach trampling.

Diazinon was microencapsulated with a polyamide-polyurea wall.[9,60,67] This MC showed superior residual effect to EC against German cockroaches. The advantage of this product is reduction of toxicity and longer residual activity. This product is also active against diazinon-resistant cockroaches. This is due to the change of mode of action by microencapsulation. Diazinon is generally known to be active by contact poison. By the massive ingestion of MC's into the digestive tracts, which is specific for MC's, diazinon MC could be active against the diazinon-resistant cockroaches.

There are also reported fenitrothion and pyrethroid (fenvalerate and fenpropathrin) MC's for agricultural use whose mode of action is via breaking of MC.[50-52,83] For the fenvalerate MC against diamondback moth (*Platella xylostella*), it was found that there was a linear relationship between the LC_{50} and D/T ratio on a log-log graph paper.[50,83] Fenitrothion MC's showed similar biological behavior as that of fenvalerate MC.[50,83] These result indicate that D/T parameter, i.e., the strength of the MC, determines its efficacy. Thus, in these cases, the crushing of the MC's by the insects is the most important process in biological efficacy.

Fish toxicity against killifish (*Oryzias latipes*)[50,83,86] and mammalian toxicity LD_{50} (mg/kg)[51,76] of pyrethroid MC's were found to depend on DT, the parameter of the release rate of a.i. into water from MC's. Therefore fish toxicity and mammalian toxicity are controlled by diffusion of the a,i. into water.

Temperature-activated MC's have been developed by utilizing side chain crystallizable polymers (SCCP) with melting point in the 15-30°C range.[6,25,25,41] SCCPs have an acrylic backbone with a series of long chain fatty alcohols esterified to it as side chains. It is the ability of these chains to crystallize and then melt over a very narrow temperature range (5°C), that allows for differential temperature release rates of the a.i. The side chain length influences the release temperature of the polymer by changing the polymer melting point (Tm). Side chain lengths of 12-18 carbon units will give release temperatures of from 15 to 30 °C.

Diazinon MC's with Tm of 30°C were prepared.[6, 26] The release rate of a.i. from MC's increased from 2.5μg/h at 20°C to 17μg/h at 32°C. The MC's gave significantly less control at 20°C, but control increased to 90% when the temperature increased to 32°C. The high level of control continued for 4-wk at 32°C. Thus, there was a higher level of control at temperatures higher than the polymer's glass transition temperature but less control below it.

Bacillus thuringiensis (Bt) was encapsulated in a starch matrix in order

to control the European corn borer.[13] Microencapsulation of pesticides in yeast was also reported.[31]

It is also expected that newer and simpler microencapsulation methods may be developed for preparing more functional microcapsules. An example is self-microencapsulation in which microcapsules are prepared merely by addition of a liquid formulation containing a wall forming monomer to water.[35,74] A sprayable, self-encapsulating starch formulation has also been developed.[65]

2. Polymeric Pesticides

Polymeric pesticides are obtained by bonding pesticides to polymers via covalent or ionic bonds to polymers. Polymeric pesticides are also obtained by binding pesticide first to monomers, followed by polymerization. Pesticide is released from the polymeric pesticide by hydrolysis or photolysis of the polymer-pesticide bond in the environment.[84]

A polymeric pesticide of chlordimeform for site-specific release control on cotton leaves was reported.[36] The following specific properties in the cotton leaf's microenvironment were to be utilized as a specific release trigger.

- pH values in the range of 8-10 existent on the leaf surfaces caused by alkaline excretions.
- the optimum orientation of the leaves to sunlight with its photochemical potency.
- cation concentration of 18-20 m moles/l found in cotton leaf dew.

Consequently, alkali-catalized hydrolysis, photolysis, and cation exchange have been identified as the most promising target-specific triggers to be utilized in the new site-specific release system for cotton. Preliminary greenhouse and field experiments have given evidence of the advantage of site-specific release systems. Especially light-triggered release as a concept showed the most promising results with respect to a remarkably prolonged duration of biological activity.

E. BIOPESTICIDE FORMULATIONS[1,2,22]

Biopesticides are based on naturally occurring toxins, and microorganisms such as fungi, bacteria, viruses, protozoa and nematodes are used in insect and weed control. Interest is growing in biological control agents because they are safe, nonpolluting, and sometimes more effective than chemical pesticides.

Microbial insecticides are extremely promising pest-control tools for use in IPM programs. Their mode of action is slower than conventional chemical insecticides. Microbiologicals are generally quite specific and therefore nontoxic to nontarget organisms, and they are less likely to cause insect resistance than are chemical insecticides.[2]

Biopesticides, however, have the problems of stability both during

storage and after application. Therefore, formulation research works are very important.

A particularly promising method to stabilize microbial insecticides is to encapsulate them in a pH-sensitive polymer that provides protection until the polymer is broken down by the high pH in the insect gut.[2,4]

After application, the microbial formulation is subject to various environmental degradation conditions such as leaf pH, leaf exudates and proteolytic enzymes, desiccation and sunlight. Microbial insecticides have been found to lose 50% of their activity within a few days by solar radiation. Optical brighteners have been found to give complete UV protection to viral insecticides.[66]

There are some other examples of microencapsulated biopesticides.[7,22,39,88] *Bacillus thuringiensis* (Bt) was microencapsulated in pre-gelatinized starch; the addition of congo red protected the Bt against UV degradation.[14,65] A sprayable self-encapsulating starch formulation was also developed. Pre-gelatinized starch, sucrose, and Bt were mixed in water, and sprayed to cotton leaves, and Bt was entrapped on the leaf surface after application. This MC had good rainfastness, and was effective against European corn borer (*Ostrinia nubilalis* Hübner) neonate larvae for more than 2 wk.[38]

Cellcap is a commercial product utilizing non-living bacterial cells of the genus *Pseudomonas fluorescense* as the walls for encapsulating the protein toxins from strains of *Bacillus thuringiensis*.[17,22,73] The bacteria are generally engineered to contain the Bt genes coding for the production of the toxins which accumulate within *Pseudomonas* cells during fermentation. The cells are then killed and stabilized, hardening the bacterial cell wall by crosslinking, and inactivation of biotoxin degrading enzymes within the cell. The process leaves the fully active biotoxin effectively encapsulated within the bacterial cell. This product showed good efficacy for diamondback moth on cabbage, partly due to the enhanced field persistence achieved by the stabilization process.[22]

Microencapsulation in living cells was also reported.[17,22] Bt toxin gene was integrated into the chromosome of *Pseudomonas fluorescense* by a gene replacement with the transposon Tn5.[49] The Tn5 transposon was made transposase minus by deleting the responsible region from the transposon and replacing it with the Bt endotoxin.

The living cell approach to biotoxin delivery has some potential advantages over non-living cells.[22] Since biotoxins such as the δ endotoxins of Bt must be ingested to be effective, it may be difficult to deliver them effectively in a non-living form to soil-bound roots. The living cells, however, can be applied to seeds prior to planting with the possibility that such cells may be able to colonize roots as the plant grows. A living cell could provide protection with only one application through a growing season.

It has been reported that biopesticides can be entrapped within a cross-linked matrix of organic polymers such as alginate, polyacrylamide, or carrageenan to form stable and uniform granules.[19] These formulations are relatively inexpensive and permit addition of nutrient bases, pesticides, or other compounds.

It is also reported that invert emulsions promote infection without a lengthy dew period, although fungi which attack weeds often require a lengthy dew period to effect infection.[5,56]

Pheromones and other attractants can be included to direct the pest to the insecticide.[90] This "attracticide" formulation can reduce amounts of insecticides.[3]

Combinations of herbicides and bacteria can significantly reduce herbicide use rate to control a broad spectrum of weed species.[8]

F. OTHER FUNCTIONAL FORMULATIONS

1. Jumbo Herbicides[32,48]

The Japan Association for Advancement of Phyto-Regulators (JAPR) has carried out basic research concerning large granular type herbicides, provisionally called Jumbo Pellet (JP), in an attempt to treat 0.3 ha paddy field within 5-6 min by throwing 20 JPs per 0.1 ha from levees into a paddy field. At present, "Jumbo" is a general term of the throw-in type herbicide formulations, and each formulation is about 50 g and applied 100-200 formulations per hectare from the levees by hand. Then they spread and diffuse easily in water. The advantages of Jumbo herbicides are as follows,

- Small and light: Dosage is 1/3 of usual application.
- Easy application and labor saving: They can be applied by hand from levees.
- Dust free and no drift: Safe for both workers and adjacent plants.
- Proper application: Depending on the area of the field, appropriate numbers of the formulations are thrown at equal distance.
- Reduced cost of rice crop: Costs of delivery and storage of the formulation becomes cheaper.
- Applicable even in bad conditions: They can be applied even on windy days.

Jumbo herbicides are classified into two types. One is on effervescent tablet type. The other is water soluble package type. Effervescent tablets are formulated by using solid acid, carbonate, and dispersants. When these tablets are put into water, they effervesce vigorously and spread over a broad area. Active ingredients spread smoothly in the paddy field and become uniform within 6-24 hr. Water-soluble bags of herbicide granules are also available.

2. Water Surface Spreading Formulations

Water surface spreading granules of cycloprothrin are formulated by

using potassium chloride as a carrier in order to control rice water weevil.[63] This formulation is made mostly by impregnation of active ingredient solution into granulated carriers. After application to the paddy field, granules sink temporarily down onto the soil. Then potassium chloride dissolves and granules resurface and float. Finally, the active ingredient solution spreads in all directions on the water surface. Rice water weevils, *Lissorhoptrus oryzophilus* live in paddy water and on rice plants, and touch the water surface. Therefore, this formulation can deliver the high concentration of the active ingredient to the place where target rice water weevils are living to result in good control. For this reason, this granule could be said to be a site-specific formulation.

Binders in the granules are very important to resurface the granules. The binders act as a trap of air in the granules after dissolution of potassium chloride in water that result in resurfacing of the granules. Therefore the binders should not dissolve completely but remain viscous and keep their binding property for some time. For such binders, a combination of high molecular weight sodium polyacrylate and xanthan gum is the best.

In order to spread the active ingredient on the water surface, organic solvents and surface active agents are used. In this case, the diisodecylphthalate is used as a solvent and use of the block copolymers of ethyleneoxide and propyleneoxide as the surfactants is appropriate.

These granules are also packaged in water-soluble bags,[37] and are applied by throwing ten, 60-g bags from levees by hand. The advantages obtained are similar to those from jumbo herbicides. When these water-soluble bags are applied to water they dissolve within a few minutes. The granules resurface for about 4 hours and the oily active ingredients spread on the water surface to control rice water weevil.

It has recently been shown that the technology using potassium chloride as the carrier allows the herbicides to spread and diffuse sufficiently over the paddy field. In this instance, a water-soluble bag is seen as being applicable for the packaging of such jumbo herbicides.

Floating carriers such as foaming perlite and silicone surfactants are also applied to help the granules float, spread and diffuse on the water surface after application in water soluble bags.[47]

A water-surface-spreading oil formulation has also been developed.[15] This formulation is put drop by drop into the paddy field from bottles, which are hung from poles. Oily active ingredients immediately spread on the water surface. The oily film adheres to leaf sheaths and leaves of the rice plant. Surface tension and capillary action assure control of the rice insects even with changes in either the water level from rain or growth of rice plant, and control insect pests of rice crop. This application method is effective even in rainy condition and it provides for substantial reductions in labor requirements.

3. 1 kg Granule[72,76-79,85]

In Japan, herbicide granules are packed in 3-kg packages that will treat 0.1 hectares. Recently, however, JAPR proposed to reduce the dosage to 1-kg /0.1-ha (1-kg granule). The 1-kg granule was developed to save application labor in paddy field and also to reduce distribution and storage charges. The 1-kg granules contain 3 times the amount of active ingredients as compared to the 3-kg granules. The 1-kg granules are designed to be spread from the levees of the paddy field which has a 30-m total width. Therefore, the particle diameter needs to be 1.0-1.5 mm (mainly 1.2mm) to reach out 15 m from each levees by the power spreader (the particle diameter of the 3-kg granules is 0.8- 0.9mm). Thus, there are about 400 granules in 1g of 1-kg granule as compared to ca. 1000 granules in 1g of 3-kg granules. This results in about 4 granules of 1-kg granules/100 cm^2 while there is 30 granules of the 3-kg material/100 cm^2. Thus the number of granules of 1 kg granules per unit area is about one eighth of that of 3 kg granules. In order to get stable herbicidal efficacy, it is essential to maximize the diffusion of the active ingredients in paddy water by either making smaller particle sizes of the active ingredients, and/or selecting of appropriate surfactants. With recent improvements, the 1-kg granules now give sufficient herbicidal efficacy.

V. CONCLUSIONS AND FUTURE TRENDS

Recent trends are moving toward developing safer pesticides, more efficient and more labor-saving formulations, and new application technologies. Therefore development of highly effective, but short-lived and biorational active ingredients at reduced dosage is essential. For this purpose, research work for pesticide delivery systems becomes important. By advance of formulation technologies, various new functional formulations have been developed along this line, which achieve targeting, improve safety for workers and environment, reduce toxicity, increase biological efficacy, and save labor in the field. For example, there have been developed the microcapsules for cockroach control, whose mode of action is trampling of the microcapsules by cockroaches, water surface spreading formulations as site-specific ones, temperature-activated microcapsules and polymeric pesticides which are activated by water, UV light, or ions. For targeting, spray nozzles with the sensors that detect the targets have also been developed. The trend is to develop more various stimuli-responsive formulations and application technologies.

Biopesticides are safe, nonpolluting, and target specific. Therefore they are very promising and will be used more widely, but their formulations must be stabilized by various methods.

The probability of discovering new pesticides through screening has decreased. It has become very difficult to develop new pesticides, and cost

and time for development of the new pesticides has increased significantly. Therefore, the development of new functional formulations and new application fields for existing pesticides is comparable to the invention of new pesticides. Thus, the cost and time required for such development would be less than that needed for the development of new pesticides. For example, fenitrothion microcapsules for termite control were recently developed. Fenitrothion is effective against termites but it decomposes on soil. Therefore, conventional formulations of fenitrothion could not be used for termite control. Microencapsulation protects fenitrothion from contact with soil and reduces decomposition. By this method, a new formulation and a new application field for fenitrothion were developed.

For labor saving, various formulations and applications methods have been developed. In these cases, formulations have been developed to integrate into their containers and application methods. There are examples where the containers themselves function as the applicators, e.g. pesticide applications from the levees and irrigation inlets in paddy fields.

In order to improve safety for workers and reduce the container disposal problem, water-soluble packages have been developed. This technology will be more widely used in future agricultural formulations. Closed transfer systems and returnable and mini-bulk containers are also used in the United States.

In the future, it is considerably desired to develop intelligent pesticide formulations and application technologies, which have sensing, processing, and activating functions. Then pesticide application will become very efficient, safe, and labor saving. Further development of these new functional formulations and application technologies are highly expected.

ACKNOWLEDGMENTS

I wish to thank Agros Corporation for permission to publish this work. I also thank Mr. H. Kobayashi for preparation of the manuscript.

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PULL HERE TO OPEN ►

Reflex®

Herbicide

For Control of Weeds in Cotton, Dry Beans, Snap Beans, and Soybeans

Active Ingredient:
Sodium salt of fomesafen
5- [2-chloro-4-(trifluoromethyl)phenoxy]-N-
(methylsulfonyl)-2-nitrobenzamide 22.8%*

Other Ingredients:	77.2%
Total:	100.0%

**Equivalent to 21.7% fomesafen or 2 pounds fomesafen active ingredient per gallon.*

KEEP OUT OF REACH OF CHILDREN.

DANGER/PELIGRO

Si usted no entiende la etiqueta, busque a alguien para que se la explique a usted en detalle. (If you do not understand the label, find someone to explain it to you in detail.)

See additional precautionary statements and directions for use inside booklet.

EPA Reg. No. 100-993 *EPA Est. 100-NE-001*

Product of China
Formulated in the USA

SCP 993A-L1C 0207

2.5 gallons
Net Contents

syngenta®

FIRST AID	
If in eyes	• Hold eye open and rinse slowly and gently with water for 15-20 minutes. • Remove contact lenses, if present, after the first 5 minutes, then continue rinsing. • Call a poison control center or doctor for treatment advice.
If swallowed	• Call a poison control center or doctor immediately for treatment advice. • Have person sip a glass of water if able to swallow. • Do not induce vomiting unless told to by a poison control center or doctor. • Do not give anything by mouth to an unconscious person.
If on skin or clothing	• Take off contaminated clothing. • Rinse skin immediately with plenty of water for 15-20 minutes. • Call a poison control center or doctor for treatment advice.
If inhaled	• Move person to fresh air. • If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably mouth-to-mouth, if possible. • Call a poison control center or doctor for further treatment advice.
NOTE TO PHYSICIAN Probable mucosal damage may contraindicate the use of gastric lavage.	
Have the product container or label with you when calling a poison control center or doctor or going for treatment.	
HOTLINE NUMBER For 24 Hour Medical Emergency Assistance (Human or Animal) Or Chemical Emergency Assistance (Spill, Leak, Fire or Accident) Call **1-800-888-8372**	

PRECAUTIONARY STATEMENTS

Hazards To Humans And Domestic Animals

DANGER

CORROSIVE. CAUSES IRREVERSIBLE EYE DAMAGE. DUE TO CORROSIVE NATURE, MAY BE HARMFUL OR FATAL IF SWALLOWED. HARMFUL IF INHALED OR ABSORBED THROUGH SKIN. Do not get in eyes, on skin or on clothing. Avoid breathing vapors or spray mist.

Personal Protective Equipment (PPE)

Applicators and other handlers must wear:

- Long-sleeved shirt and long pants
- Chemical-resistant gloves such as barrier laminate or viton
- Shoes plus socks
- Protective eyewear

Discard clothing and other absorbent materials that have been drenched or heavily contaminated with this product's concentrate. Do not reuse them. Follow manufacturer's instructions for cleaning/maintaining PPE. If no such instructions for washables, use detergent and hot water. Keep and wash PPE separately from other laundry.

When handlers use closed systems, enclosed cabs, or aircraft in a manner that meets the requirements listed in the Worker Protection Standard (WPS) for agricultural pesticides [40 CFR 170.240(d)(4-6)], the handler PPE requirements may be reduced or modified as specified in the WPS.

User Safety Recommendations

Users should:

- Wash hands before eating, drinking, chewing gum, using tobacco or using the toilet.
- Remove clothing immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing.
- Remove PPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change into clean clothing.

Environmental Hazards

Do not apply directly to water, or to areas where surface water is present, or to intertidal areas below the mean high water mark. Do not contaminate water when disposing of equipment washwaters. Do not apply when weather conditions favor drift from target area.

This chemical is known to leach through soil into groundwater under certain conditions as a result of label use. Use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in groundwater contamination.

CONDITIONS OF SALE AND LIMITATION OF WARRANTY AND LIABILITY

NOTICE: Read the entire Directions for Use and Conditions of Sale and Limitation of Warranty and Liability before buying or using this product. If the terms are not acceptable, return the product at once, unopened, and the purchase price will be refunded.

The Directions for Use of this product should be followed carefully. It is impossible to eliminate all risks inherently associated with the use of this product. Crop injury, ineffectiveness or other unintended consequences may result because of such factors as manner of use or application, weather or crop conditions, presence of other materials or other influencing factors in the use of the product, which are beyond the control of Syngenta Crop Protection, Inc. or Seller. All such risks shall be assumed by Buyer and User, and Buyer and User agree to hold Syngenta and Seller harmless for any claims relating to such factors.

Syngenta warrants that this product conforms to the chemical description on the label and is reasonably fit for the purposes stated in the Directions for Use, subject to the inherent risks referred to above, when used in accordance with directions under normal use conditions. This warranty does not extend to the use of this product contrary to label instructions, or under abnormal conditions or under conditions not reasonably foreseeable to or beyond the control of Seller or Syngenta, and Buyer and User assume the risk of any such use. SYNGENTA MAKES NO WARRANTIES OF MERCHANTABILITY OR OF FITNESS FOR A PARTICULAR PURPOSE NOR ANY OTHER EXPRESS OR IMPLIED WARRANTY EXCEPT AS STATED ABOVE.

In no event shall Syngenta or Seller be liable for any incidental, consequential or special damages resulting from the use or handling of this product. **THE EXCLUSIVE REMEDY OF THE USER OR BUYER, AND THE EXCLUSIVE LIABILITY OF SYNGENTA AND SELLER FOR ANY AND ALL CLAIMS, LOSSES, INJURIES OR DAMAGES (INCLUDING CLAIMS BASED ON BREACH OF WARRANTY, CONTRACT, NEGLIGENCE, TORT, STRICT LIABILITY OR OTHERWISE) RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT, SHALL BE THE RETURN OF THE PURCHASE PRICE OF THE PRODUCT OR, AT THE ELECTION OF SYNGENTA OR SELLER, THE REPLACEMENT OF THE PRODUCT.**

Syngenta and Seller offer this product, and Buyer and User accept it, subject to the foregoing Conditions of Sale and Limitation of Warranty and Liability, which may not be modified except by written agreement signed by a duly authorized representative of Syngenta.

DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

Do not apply this product in a way that will contact workers or other persons, either directly or through drift. Only protected handlers may be in the area during application. For any requirements specific to your State or Tribe, consult the agency responsible for pesticide regulation.

AGRICULTURAL USE REQUIREMENTS

Use this product only in accordance with its labeling and with the Worker Protection Standard, 40 CFR part 170. This Standard contains requirements for the protection of agricultural workers on farms, forests, nurseries, and greenhouses, and handlers of agricultural pesticides. It contains requirements for training, decontamination, notification, and emergency assistance. It also contains specific instructions and exceptions pertaining to the statements on this label about personal protective equipment (PPE), and restricted-entry interval. The requirements in this box only apply to uses of this product that are covered by the Worker Protection Standard.

Do not enter or allow worker entry into treated areas during the restricted entry interval (REI) of 24 hours.

PPE required for early entry to treated areas that is permitted under the Worker Protection Standard and that involves contact with anything that has been treated, such as plants, soil, or water, is:

- Coveralls
- Chemical-resistant gloves such as barrier laminate or viton
- Shoes plus socks
- Protective eyewear

GENERAL INFORMATION

Read all label directions before using.

Reflex is a selective herbicide which may be applied preplant, preemergence and/or postemergence for control and suppression of broadleaf weeds, grasses and sedges.

Reflex is generally most effective and consistent when used postemergence, working through contact action. Therefore, emerged weeds must be thoroughly covered with spray. Some bronzing, crinkling or spotting of labeled crop leaves may occur following postemergent applications, but labeled crops soon outgrow these effects and develop normally.

Optimum broad spectrum weed control is achieved by postemergent applications of Reflex to young actively growing broadleaf weeds that are not under stress from moisture, temperature, low soil fertility, mechanical or chemical injury.

Certain germinating broadleaf weeds, grasses and sedges may be controlled or suppressed by soil residual activity from either preplant, preemergent or postemergent applications if rainfall occurs shortly after application. The extent and consistency of soil activity is dependent upon soil type, ground cover at time of application, amount of rainfall and the rate of Reflex used.

APPLICATION DIRECTIONS

Drift Management

Avoiding spray drift at the application site is the responsibility of the applicator and the grower. The interaction of many equipment and weather-related factors determines the potential for spray drift. The applicator and grower must consider the interaction of equipment and weather-related factors to ensure that the potential for drift to sensitive nontarget plants is minimal.

This pesticide may only be applied when the potential for drift to adjacent sensitive areas (e.g., residential areas, bodies of water, nontarget plants) is minimal (i.e., when the wind is blowing away from the sensitive area).

Timing - Best broad spectrum postemergence control of susceptible broadleaf weeds is obtained when Reflex is applied early to actively growing weeds. This usually occurs 14 to 28 days after planting. Refer to the weed tables for specific recommendations on weed growth stages, rates, and regions.

Spray Additives - Only spray additives cleared for use on growing crops under 40 CFR 180.1001 may be used in spray mixture.

For best broad spectrum postemergence control of susceptible broadleaf weeds in Regions 2, 3, 4 and 5 (see Regional Use Maps), Reflex can be used with a minimum of 2.5% liquid nitrogen (28% or similar) or a minimum of 10 pounds ammonium sulfate per 100 gallons of spray volume.

For Postemergence Applications Always Add One Of The Following Except In Tank Mix With Products Prohibiting Spray Additives (see Tank Mix Directions for Use):

Nonionic Surfactant (NIS) - Use NIS containing at least 75% surface active agent at 0.25 to 0.5% (1/2 to 1 pint per 25 gallons) of the finished spray volume (use in Region 1 and East of Interstates 79 and 77 for Regions 2 and 3.)

Crop Oil Concentrate (COC) - Use a nonphytotoxic COC or a once-refined vegetable oil concentrate (VOC, MSO) containing 15-20% approved emulsifier, at 0.5-1% (1-2 pints per 25 gallons) of the finished spray volume. COC can improve weed control but may slightly reduce crop tolerance.

Other Adjuvants - Adjuvants other than COC or NIS may be used providing the product meets the following criteria:

1. Contains only EPA exempt ingredients.
2. Is nonphytotoxic to the target crop.
3. Is compatible in mixture. (May be established through a jar test.)
4. Is supported locally for use with Reflex on the target crop through proven field trials and through university and extension recommendations.

Note: No adjuvants are needed for preplant or preemergence applications unless Reflex is being used in a burndown.

Recommended Mixing Order:

1. Half required amount of water, begin agitation.*
2. Dry pesticide formulations.
3. Reflex Herbicide.
4. Liquid pesticide formulation.
5. Adjuvant (COC or NIS) and fertilizer.

*Compatibility agent, 1 gallon/500 gallons of water or 0.2% v/v, may be added as needed.

GROUND APPLICATION - Use sufficient spray volume and pressure to ensure complete coverage of the target. A spray volume of 10-20 gallons per acre and 30-60 psi at the nozzle tip is recommended. On large weeds and/or dense foliage, use 60 psi and a minimum of 20 gallons per acre to ensure coverage of weed foliage.

The use of flat fan nozzles will result in the most effective application of Reflex. Use nozzles that are set up to deliver medium quality spray (ASAE Standard S-572).

DO NOT USE FLOOD TYPE OR OTHER SPRAY NOZZLES, WHICH DELIVER COARSE, LARGE DROPLET SPRAYS.

DO NOT APPLY THIS PRODUCT THROUGH ANY TYPE OF IRRIGATION SYSTEM.

BAND APPLICATIONS - Thorough weed coverage is important for postemergent control. Best coverage is obtained with a minimum of two nozzles, one directed to each side of the planted row. Application with a single nozzle directed over the top of the row is not recommended for postemergence applications but is suitable for preemergence applications. Cultivation of untreated areas may be needed following band applications. When making postemergence band applications and cultivating in the same operation, position nozzles in advance of the cultivation device. This will reduce dust in the spray area. Dust can intercept spray, reducing weed coverage, resulting in less than adequate weed control.

Calculate the amount of herbicide and water volume needed for postemergence band treatment by the following formulas:

$\frac{\text{Band width in inches}}{\text{row width in inches}}$	X	broadcast rate per acre	=	Band herbicide rate per acre
$\frac{\text{Band width in inches}}{\text{row width in inches}}$	X	broadcast volume per acre	=	Band water volume per acre

AERIAL APPLICATION - Use sufficient spray volume and pressure to ensure complete coverage of the target. A minimum of 5 gallons per acre of spray mixture should be applied with a maximum of 40 PSI pressure. When broadleaf weed foliage is dense, use a minimum of 10 gallons per acre to ensure coverage of weed foliage.

CULTIVATION - Cultivation prior to application is not recommended. Cultivation may put weeds under stress, reducing weed control. Timely cultivation 1-3 weeks after applying Reflex may assist weed control.

PRECAUTIONS

- A maximum of 1.5 pts. of Reflex Herbicide **(or a maximum of 0.375 lb. a.i./A of fomesafen from any product containing fomesafen)** may be applied per acre per year in Region 1 (see Regional Use Map).
- A maximum of 1.5 pts. of Reflex Herbicide **(or a maximum of 0.375 lb. a.i./A of fomesafen from any product containing fomesafen)** may be applied per acre in ALTERNATE years in Region 2 (see Regional Use Map).
- A maximum of 1.25 pts. of Reflex Herbicide **(or a maximum of 0.313 lb. a.i./A of fomesafen from any product containing fomesafen)** may be applied per acre in ALTERNATE years in Region 3 (see Regional Use Map).
- A maximum of 1 pt. of Reflex Herbicide **(or a maximum of 0.25 lb. a.i./A of fomesafen from any product containing fomesafen)** may be applied per acre in ALTERNATE years in Region 4 (see Regional Use Map).
- A maximum of 0.75 pt. of Reflex Herbicide **(or a maximum of 0.1875 lb. a.i./A of fomesafen from any product containing fomesafen)** may be applied per acre in ALTERNATE years in Region 5 (see Regional Use Map).
- Thoroughly clean the spray system with water and a commercial tank cleaner before and after each use.
- Tank mixes of Reflex Herbicide with other pesticides, fertilizers or any other additives except as specified on this label or other approved Syngenta supplemental labels may result in tank-mix incompatibility, unsatisfactory performance or unsatisfactory crop injury.
- Reflex Herbicide requires a 1-hour rain-free period for best results when applied postemergence.
- Apply postemergence to actively growing weeds. Avoid applying Reflex to weeds or labeled crops which are under stress from moisture, temperature, low soil fertility, mechanical or chemical injury, as reduced weed control and/or increased crop injury may result.
- Avoid overlapping spray swaths, as injury may occur to rotational crops.
- To provide adequate coverage, it is recommended that ground speed not exceed 10 mph during application.
- Do not graze treated areas or harvest for forage or hay.
- Avoid drift to all other crops and nontarget areas. Crops other than those labeled may be severely injured by drift. Do not apply when wind velocity exceeds 15 mph.
- Do not make ground or aerial application during temperature inversions.

ROTATIONAL CROP RESTRICTIONS

The following rotational crops may be planted after applying Reflex at recommended rates:

Crop To Be Planted	Minimum Rotation Interval (Months After Last Reflex Application)
Dry beans, snap beans, soybeans and cotton	0
Small grains such as wheat, barley, rye	4
Corn*, peanuts, peas, rice	10
To avoid crop injury do not plant alfalfa, sunflowers, sugar beets, sorghum** or any other crop within	18

Do not graze rotated small grain crops or harvest forage or straw for livestock. In the event of a crop loss due to weather conditions cotton, dry beans, snap beans or soybeans can be replanted.

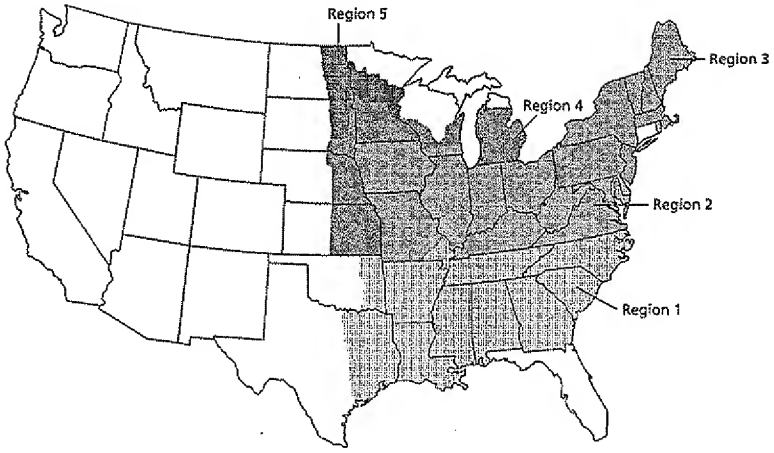
*Use a 12 month minimum rotation interval for popcorn in the states of Ohio, Kentucky, Illinois, Indiana, Iowa, and Region 4 when applied at rates of 1.0 pints per acre or more.

*Use 18 month minimum rotation interval for sweet corn in the states of Connecticut, Maine, Massachusetts, New Hampshire, New York, Rhode Island, Vermont and Region 5.

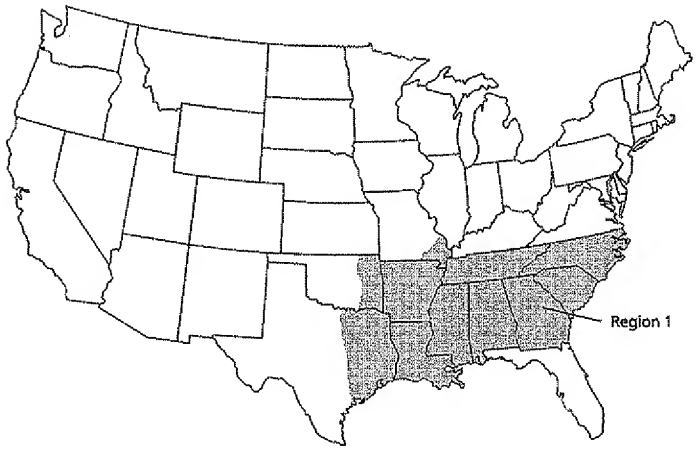
**Sorghum may be planted back after 10 months in Region 1.

USE RATES AND WEEDS CONTROLLED

REFLEX REGIONAL USE MAP



REGION 1
(Maximum Rate 1.5 pts./A per year)

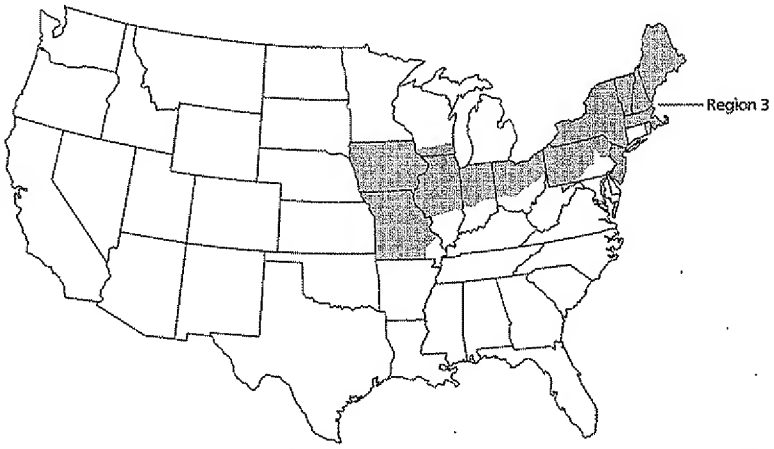


REGION 1 - Includes the following states or portion of states where Reflex may be applied: Alabama, Arkansas, Georgia, Louisiana, Mississippi, Missouri (counties of Bollinger, Butler, Cape Giradeau, Dunklin, Madison, Mississippi, New Madrid, Pemiscot, Perry, Ripley, Scott, Stoddard and Wayne), North Carolina, Oklahoma (East of U.S. Highway 75 and East of Indian Nation Parkway), South Carolina, Tennessee, and Texas (includes area East of U. S. Highway 77 to State Road 239 including all of Calhoun County).

REGION 2
(Maximum Rate 1.5 pts./A, alternate years)

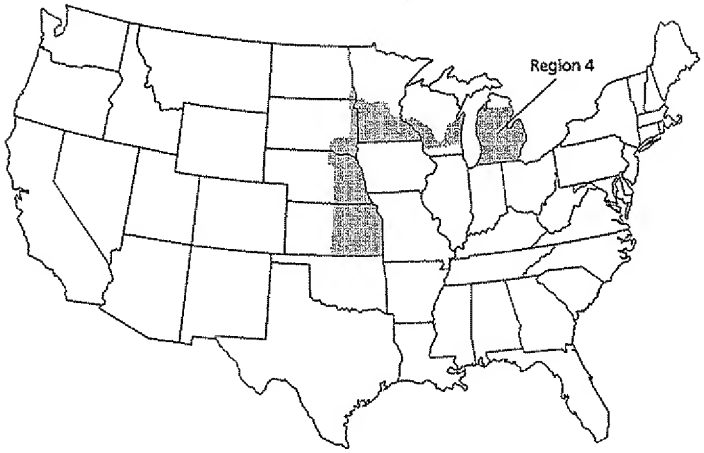
REGION 2 - Includes the following states or portion of states where Reflex may be applied: Delaware, Kentucky, Maryland, Virginia, West Virginia, South of Interstate 70 in the following states: Illinois, Indiana and Ohio and all areas South of Interstate 80 to the intersection of U.S. Highway 15 and East of U.S. Highway 15 and U.S. Highway 522 in Pennsylvania.

REGION 3
(Maximum Rate 1.25 pts./A, alternate years)



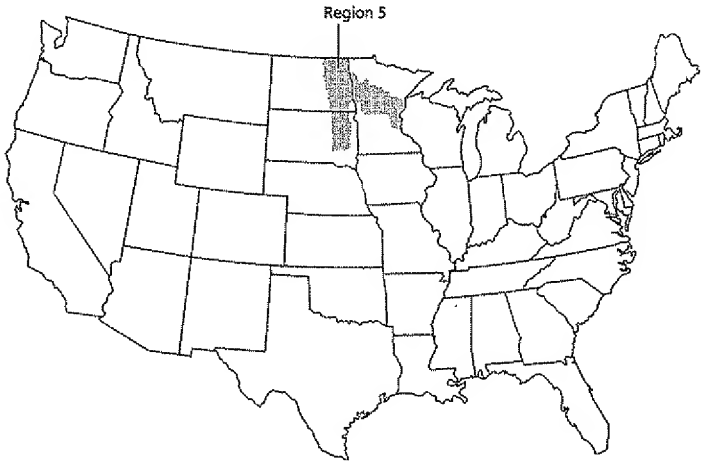
REGION 3 - Includes the following states or portion of states where Reflex may be applied: Connecticut, Iowa, Maine, Massachusetts, Missouri (all counties except for those listed in Region 1), New Hampshire, New Jersey, New York, Pennsylvania (all areas except those listed in Region 2), Rhode Island, Vermont and Wisconsin (South of U.S. Highway 18 between Prairie Du Chien and Madison, and South of Interstate 94 between Madison and Milwaukee), and North of Interstate 70 in following states: Indiana, Illinois and Ohio.

REGION 4
(Maximum Rate 1 pint per acre, alternate years)



REGION 4 - Includes the following states or portion of states where Reflex may be applied: Kansas (all counties East of or intersected by U.S. Highway 281), Michigan (Southern Peninsula), Minnesota (all areas South of Interstate 94), Nebraska (all counties East of or intersected by U.S. Highway 281), and Wisconsin (all areas, except those in Region 3, South of Interstate 94 from Minnesota state line to Eau Claire and South of U.S. Highway 29 from Eau Claire to Green Bay plus Door and Kewaunee counties. The following counties are excluded: Clark, Marathon, Wood, Portage, Adams, Shawano, Waupaca, Waushara and Marquette). North Dakota (all areas East of Interstate 29 from Fargo South to the South Dakota state line). South Dakota (all areas East of Interstate 29 from the North Dakota state line to Watertown, all areas East of Highway 81 from Watertown to Madison and all areas East and South of State Road 34 and U.S. Highway 281 to the Nebraska state line).

REGION 5
(Maximum Rate 0.75 pint per acre, alternate years)



REGION 5 - Includes the following states or portion of states where Reflex may be applied: North Dakota (all areas East of U.S. Highway 281 except those areas in Region 4), South Dakota (all areas East of U.S. Highway 281 except those areas in Region 4) and Minnesota (all areas South of U.S. Highway 2 except those areas in Region 4).

APPLICATION RATES FOR WEED GROWTH STAGES

Weed	Reflex Rate (Pts/A)			
	Maximum Growth Stage Controlled At			
	3/4 pt./A No. of True Leaves	1 pt./A No. of True Leaves	1.25 pts./A No. of True Leaves	1.5 pts./A No. of True Leaves
Anoda, Spurred	--	--	--	2
Balloonvine	--	--	2[c]	2
Carpetweed	--	6" Diameter Size	Multi-leaf 6" Diameter	Unlimited Size
Citron (Wild Watermelon)	--	2	2	4
Cocklebur, Common[a,b,d]	--	-	2	4
Copperleaf, Hophornbeam[d]	--	2	2	4
Copperleaf, Virginia	--	2	2	4
Crotalaria, Showy	--	4	4	6
Croton, Tropic[d]	--	2	2	4
Cucumber, Volunteer	--	4	4	6
Eclipta	--	2	2	4
Groundcherry, Cutleaf	--	4	4	6
Hemp[b]	--	--	4	6
Horsenettle[b]	--	2[c]	3[c]	4[c]
Jimsonweed[d]	2	4	6	8
Ladysthumb	--	2	2	4
Lambsquarters, Common[c]	--	2	2	2
Mexicanweed	--	2[c]	2[c]	2
Morningglory[d]				
Cypressvine	--	4	4	6
Entireleaf var.	2[c]	2	2	4
Ivyleaf	2[c]	2	2	4
Purple Moonflower	--	2	4	4
Red (Scarlet)	--	2	2	4
Smallflower	--	2	2	4
Pitted (Smallwhite)	--	4	4	4
Tall (Common)	2[c]	2	2	3
Palmleaf (Willowleaf)	--	2	2	4
Mustard, Wild	2	4	6	8
Nightshade, Black	2	4	4	4
Nutsedge, Yellow[d]	--	--	--	Suppression Only
Pigweed, spp.[d]				
Amaranth, Palmer	2[c]	4	4	6
Amaranth, Spiny	2[c]	2	2	4
Redroot	2[c]	4	6	6
Smooth	2[c]	4	4	6
Waterhemp, Common	2[c]	2	2	4
Waterhemp, Tall	2[c]	2	2	4
Poinsettia, Wild	--	--	--	3
Purslane, Common	--	Multi-Leaf 6" Diameter	Multi-Leaf 6" Diameter	Multi-Leaf 8" Diameter
Pusley, Florida	--	--	--	2
Ragweed, Common[d]	2	4	4	6
Ragweed, Giant[b]	--	--	4	4

Weed	Reflex Rate (Pts/A)			
	Maximum Growth Stage Controlled At			
	3/4 pt./A No. of True Leaves	1 pt./A No. of True Leaves	1.25 pts./A No. of True Leaves	1.5 pts./A No. of True Leaves
Redweed	--	--	--	3[c]
Sesbania, Hemp	--	6	6	12
Sicklepod	--	--	--	Cotyledon[c]
Sida, Prickly[d]	--	--	--	Cotyledon[c]
Smartweed, Pennsylvania	2[c]	4	4	6
Smellmelon	--	--	--	2
Spurge, Prostrate	--	--	--	1" Diameter[c]
Spurge, Spotted	--	--	--	2[c]
Starbur, Bristly	--	2	2	4
Sunflower, Common	--	--	--	2
Velvetleaf[b]	--	--	2	4
Venice Mallow	2	4	4	6
Witchweed	--	Multi-leaf Up to 7"	Multi-leaf Up to 7"	Multi-leaf Up to 10"
Yellow Rocket	2	4	6	6

[a] Do not apply in cotyledon stage.
[b] It is necessary to use 1% MSO and 2.5% UAN v/v as an adjuvant in Regions 2 and 3.
[c] Suppression only.
[d] Reflex may provide preemergence activity at 1-1.5 pints/A.

SPECIAL USE DIRECTIONS FOR ADDITIONAL WEED PROBLEMS

Suppression of Annual Grasses

The grasses listed below may be suppressed by postemergence applications and controlled or suppressed by preemergence applications of Reflex at 1 to 1½ pints/acre. Consult Use Rate Table for maximum rate in each region. For full-season broad-spectrum annual grass control, consult tank mix section.

Barnyardgrass
Broadleaf Signalgrass
Crabgrass
Foxtail
  Giant
  Green
  Yellow
Goosegrass
Johnsongrass, Seedling
Panicum, Fall
Panicum, Texas

Suppression of Perennial Weeds

Use of Reflex postemergence at rates of 1-1.5 pts./A will aid in suppressing the above-ground portions of the weeds listed below until crop canopy can assist in suppression. Perennial weeds continue to regrow from underground rootstocks even if above-ground foliage is temporarily controlled or retarded. Even though Reflex and crop competition can suppress perennial weeds for a growing season, the rootstocks will continue to live and reestablishment will occur in subsequent years.

Milkweed, Climbing
Milkweed, Honeyvine
Bindweed, Field
Bindweed, Hedge
Trumpetcreeper

CROP USE DIRECTIONS

COTTON

Preemergence

Apply Reflex preemergence at 1-1.5 pints per acre in cotton. Apply as a preemergence treatment only to coarse textured soils (sandy loam, loamy sand, sandy clay loam). **Do not** apply as a preemergence treatment to medium or fine-textured soils as crop injury will likely occur.

Apply preemergence as a broadcast or banded treatment in a minimum of 10 gallons spray solution per acre. Adequate rainfall or irrigation within 7 days of application is required for Reflex activation. Preemerge applications of Reflex will provide improved residual control of difficult to control weeds such as wild poinsettia, eclipta, cocklebur, morningglory species, prickly sida, velvetleaf, lambsquarter, spurred anoda, common ragweed and pigweed species (including herbicide resistant *Palmer amaranth*). Reflex is effective on yellow nutsedge tubers prior to emergence. The extent of yellow nutsedge activity is dependent upon the time lapsed between tillage and application and between application and rainfall or irrigation.

To broaden the weed control spectrum, Reflex may be tank mixed with other preemergence herbicides such as Caparol®, Cotoran®, Direx®, Dual MAGNUM®, Karmex®, Staple®, or Zorial®. For control of emerged weeds, Reflex may be tank mixed with a burndown herbicide such as Gramoxone® Max, Gramoxone Inteon™ or glyphosate brands (such as Touchdown®, Roundup®) labeled in cotton. In reduced tillage plantings, Reflex can be applied up to 14 days prior to planting or at planting with a burndown herbicide. Refer to the tank-mix partner label for use directions, restrictions and limitations. The most restrictive labeling applies.

Cotton plants are tolerant to preemergence applications of Reflex when applied at recommended rates. Some crinkling or spotting of cotton foliage or stunting may occur, especially if heavy rainfall occurs during or soon after cotton emergence, but cotton plants normally outgrow these effects and develop normally.

Cotton foliage is not tolerant to Reflex. Do not apply Reflex over the top of emerged cotton as unacceptable cotton injury will occur.

Do not apply more than 1.5 pints per acre of Reflex in any year.

Post-Directed Application

Apply Reflex in emerged cotton as a post-directed treatment using precision post-directed, hooded or shielded application equipment to provide complete coverage of emerged weeds. Apply Reflex at 1-1.5 pints per acre in a minimum of 10 gallons spray solution per acre. Applications may be made broadcast or banded. Post-directed applications of Reflex will provide contact control of labeled emerged weeds and residual preemergence control of labeled weeds (once activated by rainfall or irrigation). See previous label sections for a list of weeds controlled, recommended application rates, weed growth stages, and application directions.

Reflex should be applied with a non-ionic surfactant at 0.25 to 0.5% v/v, or crop oil concentrate at 1% v/v to emerged weeds. Do not add liquid nitrogen (28% or similar) to Reflex, or Reflex tank mixes in cotton.

Always apply Reflex under favorable environmental conditions that promote active weed growth. Emerged weeds should be actively growing and not under stress due to drought, extreme temperatures, excessive water or low humidity.

To broaden the weed control spectrum, post-directed applications of Reflex may be tank mixed with other labeled post-directed herbicides such as Caparol, DSMA, Direx, Dual MAGNUM, Envoke®, Karmex, Layby™ Pro, MSMA, Sequence®, or Suprend®. When applied with hooded or shielded sprayers, Reflex and Reflex tank mixes may be applied with burndown products such as Gramoxone Max, Gramoxone Inteon, Sequence or glyphosate brands (such as Touchdown, Roundup) labeled for in crop application in cotton. Refer to the tank mix partner label for use directions, restrictions and limitations. The most restrictive labeling applies.

Cotton foliage is not tolerant to Reflex applications. Avoid contact to cotton foliage as unacceptable injury will occur. Application equipment should be calibrated (spray pressure, nozzle type and configuration, and orifice size) to avoid fine spray droplets contacting green stems or cotton foliage.

Post-Directed Application Timing in Cotton

Reflex may be applied to cotton at least 6 inches in height through lay-by as a post-directed application. All post-directed applications should avoid spray contact with any green non-barked parts of the cotton plant or foliage as unacceptable injury will occur. Follow the application timing recommendations below for post-directed applications in cotton.

Shield and Hooded Applications

Make a precision post-directed Reflex application to the base of the cotton plant avoiding contact with the cotton stem or foliage when cotton is at least 6 inches in height with less than 4 inches of brown bark. Use only hooded or shielded spray equipment to apply Reflex in cotton that is 6 inches to 12 inches in height. Adjust nozzles to provide full coverage of emerged target weeds.

Layby Applications

Make a post-directed Reflex application to the base of the cotton plant avoiding contact with any non-barked portion of the cotton plant or foliage. Use precision post-directed equipment or hooded or shielded sprayers on cotton that has developed a minimum of 4 inches of brown bark through lay-by. Application equipment should be configured to provide full coverage of emerged target weeds.

Do not apply Reflex later than 70 days before harvest.

Do not apply more than 1.5 pints per acre of Reflex in any year.

Suppression of Woollyleaf Bursage (Lakeweed), *Ambrosia grayi*, in Texas

Apply Reflex to cultivated areas of cropland in the fall or spring as a spot treatment at a rate of 1.5 pints per acre and incorporate to a depth of 2-3 inches for suppression of woollyleaf bursage. Applications should be made with ground equipment only in a minimum of 10 gallons of water per acre using 20-40 psi at the nozzle tip. Significant suppression may not be seen until 6-8 months after application, but should then continue for at least 2 years after application.

The use of adjuvants, as specified under **General Information** of the Reflex label, will significantly improve the initial burndown of any emerged woollyleaf bursage, but this effect is only temporary. Therefore, an adjuvant may be used if desired, but is not necessary.

Cotton or soybean may be planted in treated areas. Under certain conditions, significant damage may occur to cotton planted within 18 months of application. A 3-year interval from last application to planting is required for all other crops.

Do not make more than one application of Reflex per year. Do not apply more than 1.5 pints per acre of Reflex in any year. If two consecutive year applications are made, allow a 2 year interval before another application.

DRY BEANS

Apply Reflex as a postemergent broadcast application for control or suppression of weeds listed in the **Application Rates For Weed Growth Stages** table and **Special Use Directions For Additional Weed Problems.** Application rate depends on weed growth stage, but not to exceed the maximum rate specified per geographic region (Refer to Map For Definition of Specified Geographic Regions). Refer to the **Spray Additive** section and include in the application when the beans have at least one fully expanded trifoliate leaf. Do not use liquid nitrogen (28% or similar) on dry beans. Two applications may be made if necessary but the total yearly dose does not exceed 1.5 pints (0.375 lbs. active) per acre.

Do not exceed 1.5 pints (0.375 lbs.) per acre in any one year. Do not apply to any field in Regions 2, 3, 4, or 5 more than once every two years. Do not graze animals on green forage or stubble. Do not utilize hay or straw for animal feed or bedding. Do not apply within 45 days of harvest.

Tank Mix and Sequential Applications

Reflex can be used sequentially or in tank mix with the following products: Assure II®, Basagran®, Dual MAGNUM, Eptam®, Frontier®, Poast®, Prowl®, Pursuit®, Raptor®, Select®, Sonalan®, or Treflan®.

Under certain conditions, the mixture of Reflex with one or more of the above mentioned broadleaf herbicides may cause a reduction in activity of any postemergence grass herbicide in the mixture.

For sequential applications allow 2-3 days after the application of the grass herbicide before applying Reflex or Reflex mixtures. Where Reflex or the Reflex mixture is applied first, apply the grass herbicide when the grass weeds begin to develop new leaves (generally around 7 days).

NOTE: Tank mix applications can result in increased crop injury as compared to either product used alone.

SNAP BEANS

Apply Reflex as a postemergent broadcast application for control or suppression of weeds listed in the **Application Rates For Weed Growth Stages** table and **Special Use Directions For Additional Weed Problems.** Application rate depends on weed growth stage, but not to exceed the maximum rate specified per geographic region (Refer to Map For Definition of Specified Geographic Regions). Apply with NIS, COC or other adjuvant when the snap beans have at least one fully expanded trifoliate leaf. Do not use liquid nitrogen (28% or similar) on snap beans. Two applications may be made if necessary but the total yearly dose does not exceed 1.5 pints (0.375 lbs. active) per acre.

Do not exceed 1.5 pints (0.375 lbs. active) per acre in any one year. Do not apply to any field in Regions 2, 3, 4, or 5 more than once every two years. Do not graze treated areas or harvest for forage or hay. Do not utilize hay or straw for animal feed or bedding. Do not apply within 30 days of harvest.

Tank Mix and Sequential Applications

Reflex can be used sequentially or in tank mix with the following products: Assure II, Basagran, Dual MAGNUM, Eptam, Poast, Prowl, Pursuit, Raptor or Treflan.

Under certain conditions, the mixture of Reflex with one or more of the above mentioned broadleaf herbicides may cause a reduction in activity of any postemergence grass herbicide in the mixture.

For sequential applications allow 2-3 days after the application of the grass herbicide before applying Reflex or Reflex mixtures. Where Reflex or the Reflex mixture is applied first, apply the grass herbicide when the grass weeds begin to develop new leaves (generally around 7 days).

NOTE: Tank mix applications can result in increased crop injury as compared to either product used alone.

SOYBEANS

Reflex Alone

Apply Reflex either preplant, preemergence, or postemergence using the appropriate rate for geographical region, weed spectrum, and stage of growth.

Preplant Surface Applied or Preemergence

Apply Reflex preplant surface or preemergence in Regions 1, 2, 3, and 4 at a rate not exceeding the maximum lbs./A. If weeds are present at the time of application, add a burndown herbicide.

Certain germinating broadleaf weeds, grasses, and sedges may be controlled or suppressed by soil residual activity if rainfall occurs shortly after application. The extent and consistency of soil activity is dependent on soil type, ground cover at time of application, amount of rainfall and rate of Reflex used.

Postemergence

Apply Reflex postemergence for control of weeds listed in the **Application Rates For Weed Growth Stages** according to the rate limits specified per regional map. Emerged weeds must be thoroughly covered with spray. Some bronzing, crinkling or spotting of soybean leaves may occur following postemergent applications, but soybeans soon outgrow these effects and develop normally.

Do not apply within 45 days of harvest.

Tank Mix and Sequential Applications For Soybeans

Reflex can be used sequentially or in tank mix with one or more of the following products: Assure II, Basagran, Butyrac®, Classic®, FirstRate®, Fusilade® DX, Fusion®, Glyphosate (such as Touchdown, Roundup or Glyphomax), Gramoxone Max, Harmony® GT, Harmony® GT XP, Pursuit, Poast, Poast Plus®, Raptor, Resource®, Select, Scepter®, and Synchrony® STS®.

Under certain conditions, the mixture of Reflex with one or more of the above mentioned broadleaf herbicides may cause a reduction in activity of any postemergence grass herbicide in the mixture.

For sequential applications allow 2-3 days after the application of the grass herbicide before applying Reflex or Reflex mixtures. In case Reflex or the Reflex mixture is applied first, apply the grass herbicide when the grass weeds begin to develop new leaves (generally around 7 days).

NOTE:

- Tank-mix applications can result in increases in crop injury as compared to either product used alone.
- Do not exceed 1 fl. oz. of Butyrac per acre in mixture with Reflex.
- Do not exceed 0.25 oz./A of Synchrony STS herbicide in the tank with labeled rates of Reflex on non-STS varieties. This tank mix can be applied postemergence to any soybean variety for additional broadleaf weed control. Refer to the Synchrony STS label for more information and crop rotation restrictions.
- Always read and follow the recommendations, restrictions and limitations for all products whether used alone, sequentially or in a tank mix. The most restrictive labeling of any product used applies.

Roundup Ready® Soybean Tank Mixes

Reflex at 6-12 oz./A, can be tank mixed with glyphosate products (such as Touchdown or Roundup) that are labeled for Roundup Ready Soybeans for improved postemergence control of many weeds such as morningglory spp., hemp sesbania, waterhemp, and black nightshade which are known to have tolerance to glyphosate, but are susceptible to Reflex.

FOLLOW THE RECOMMENDATIONS ON THE GLYPHOSATE PRODUCT LABEL FOR THE USE OF SPRAY ADDITIVES IN THIS TANK MIX.

Do not allow this tank mix to move off target as contact by even minute quantities can cause severe damage or death to any non-target vegetation.

NOTE: Postemergence application of this tank mix on soybean varieties which do not contain the Roundup Ready gene will result in severe crop injury or death of the soybean crop. Always read and follow the recommendations, restrictions and limitations for all products used. The most restrictive labeling of any product applies.

AERIAL SPRAY DRIFT MANAGEMENT ADVISORY

SPRAY DRIFT MANAGEMENT

AVOIDING SPRAY DRIFT AT THE APPLICATION SITE IS THE RESPONSIBILITY OF THE APPLICATOR. The interaction of many equipment and weather related factors determine the potential for spray drift. The applicator and the grower are responsible for considering all these factors when making decisions.

The following drift management requirements must be followed to avoid off-target drift movement from aerial applications to agricultural field crops. These requirements do not apply to forestry applications, public health uses or to applications using dry formulations.

1. The distance of the outer most nozzles on the boom must not exceed 3/4 the length of the wingspan or rotor.
2. Nozzles must always point backward parallel with the air stream and never be pointed downwards more than 45 degrees.

Where states have more stringent regulations, they should be observed.

The applicator should be familiar with and take into account the information covered in the **Aerial Drift Reduction Advisory Information.**

Aerial Drift Reduction Advisory Information

IMPORTANCE OF DROPLET SIZE

The most effective way to reduce drift potential is to apply large droplets. The best drift management strategy is to apply the largest droplets that provide sufficient coverage and control. Applying larger droplets reduces drift potential, but will not prevent drift if applications are made improperly, or under unfavorable environmental conditions (See **Wind, Temperature and Humidity,** and **Temperature Inversion** sections of this label).

CONTROLLING DROPLET SIZE

- **Volume** - Use high flow rate nozzles to apply the highest practical spray volume. Nozzles with higher rated flows produce larger droplets.
- **Pressure** - Use the lower spray pressures recommended for the nozzle. Higher pressure reduces droplet size and does not improve canopy penetration. When higher flow rates are needed, use higher flow rate nozzles instead of increasing pressure.
- **Number of nozzles** - Use the minimum number of nozzles that provide uniform coverage.
- **Nozzle Orientation** - Orienting nozzles so that the spray is released backwards, parallel to the airstream will produce larger droplets than other orientations. Significant deflection from horizontal will reduce droplet size and increase drift potential.
- **Nozzle Type** - Use a nozzle type that is designed for the intended application. With most nozzle types, narrower spray angles produce larger droplets. Consider using low-drift nozzles. Solid stream nozzles oriented straight back produce larger droplets than other nozzle types.

BOOM LENGTH

For some use patterns, reducing the effective boom length to less than 3/4 of the wingspan or rotor length may further reduce drift without reducing swath width.

APPLICATION HEIGHT

Applications should not be made at a height greater than 10 feet above the top of the target plants unless a greater height is required for aircraft safety. Making applications at the lowest height that is safe reduces exposure of droplets to evaporation and wind.

SWATH ADJUSTMENT

When applications are made with a crosswind, the swath will be displaced downwind. Therefore, on the up and downwind edges of the field, the applicator must compensate for this displacement by adjusting the path of the aircraft upwind. Swath adjustment distance should increase with increasing drift potential (higher wind, smaller drops, etc.).

WIND

Drift potential is lowest between wind speeds of 2-10 mph. However, many factors, including droplet size and equipment type determine drift potential at any given speed. Application should be avoided below 2 mph due to variable wind direction and high inversion potential. **NOTE:** Local terrain can influence wind patterns. Every applicator should be familiar with local wind patterns and how they affect spray drift.

TEMPERATURE AND HUMIDITY

When making applications in low relative humidity, set up equipment to produce larger droplets to compensate for evaporation. Droplet evaporation is most severe when conditions are both hot and dry.

TEMPERATURE INVERSIONS

Applications should not occur during a temperature inversion because drift potential is high. Temperature inversions restrict vertical air mixing, which causes small suspended droplets to remain in a concentrated cloud. This cloud can move in unpredictable directions due to the light variable winds common during inversions. Temperature inversions are characterized by increasing temperatures with altitude and are common on nights with limited cloud cover and light to no wind. They begin to form as the sun sets and often continue into the morning. Their presence can be indicated by ground fog; however, if fog is not present, inversions can also be identified by the movement of smoke from a ground source or an aircraft smoke generator. Smoke that layers and moves laterally in a concentrated cloud (under low wind conditions) indicates an inversion, while smoke that moves upward and rapidly dissipates indicates good vertical air mixing.

SENSITIVE AREAS

The pesticide should only be applied when the potential for drift to adjacent sensitive areas (e.g. residential areas, bodies of water, known habitat for threatened or endangered species, nontarget crops) is minimal (e.g. when wind is blowing away from the sensitive areas).

APPENDIX

Scientific names are listed for those weeds referred to in the Reflex label.

COMMON NAME	SCIENTIFIC NAME
Amaranth, Palmer	*Amaranthus palmeri*
Amaranth, Spiny	*Amaranthus spinosus*
Anoda, Spurred	*Anoda cristata*
Balloonvine	*Cardiospermum halicacabum*
Barnyardgrass	*Echinochloa crus-galli*
Bindweed, Field	*Convolvulus arvensis*
Bindweed, Hedge	*Calystegia sepium*
Broadleaf Signalgrass	*Brachiaria platyphylla*
Carpetweed	*Mollugo verticillata*
Citron (Wild Watermelon)	*Citrullus vulgaris*
Cocklebur, Common	*Xanthium strumarium*
Copperleaf, Hophornbeam	*Acalypha ostryifolia*
Copperleaf, Virginia	*Acalypha virginica*
Crabgrass	*Digitaria spp.*
Crotalaria, Showy	*Crotalaria spectabilis*
Croton, Tropic	*Croton glandulosus*
Cucumber, Volunteer	*Cucumis sativas*
Eclipta	*Eclipta prostrata*
Foxtail, Giant	*Setaria faberi*
Foxtail, Green	*Setaria viridis*
Foxtail, Yellow	*Setaria glauca*
Goosegrass	*Eleusine indica*
Groundcherry, Cutleaf	*Physalis angulata*
Hemp	*Cannabis sativa*
Horsenettle	*Solanum carolinense*
Jimsonweed	*Datura stramonium*
Johnsongrass, Seedling	*Sorghum halepense*
Ladysthumb	*Polygonum persicaria*
Lambsquarters, Common	*Chenopodium album*
Mexicanweed	*Caperonia castaniifolia*
Milkweed, Climbing	*Sarcostemma cyanchoides*
Milkweed, Honeyvine	*Ampelamus albidus*
Morningglory, Cypressvine	*Ipomoea quamoclit*
Entireleaf	*Ipomoea hederacea var. integriuscula*
Ivyleaf	*Ipomoea hederacea var. hederacea*
Purple Moonflower	*Ipomoea turbinata*
Red (Scarlet)	*Ipomoea coccinea*
Smallflower	*Jacquemontia tamnifolia*
Pitted (Smallwhite)	*Ipomoea lacunosa*
Tall (Common)	*Ipomoea purpurea*
Palmleaf (Willowleaf)	*Ipomoea wrightii*
Mustard, Wild	*Brassica kaber*
Nightshade, Black	*Solanum nigrum*
Nutsedge, Yellow	*Cyperus esculentus*
Panicum, Fall	*Panicum dichotomiflorum*
Panicum, Texas	*Panicum texanum*

COMMON NAME	SCIENTIFIC NAME
Pigweed, Redroot	*Amaranthus retroflexus*
Pigweed, Smooth	*Amaranthus hybridus*
Poinsettia, Wild	*Euphorbia heterophylla*
Purslane, Common	*Portulaca oleracea*
Pusley, Florida	*Richardia scabra*
Ragweed, Common	*Ambrosia artemisiifolia*
Ragweed, Giant	*Ambrosia trifida*
Redweed	*Melochia corchorifolia*
Sesbania, Hemp	*Sesbania exaltata*
Sicklepod	*Cassia obtusifolia*
Sida, Prickly	*Sida spinosa*
Smartweed, Pennsylvania	*Polygonum pennsylvanicum*
Smellmelon	*Cucumis melo*
Spurge, Prostrate	*Euphorbia humistrata*
Spurge, Spotted	*Euphorbia maculata*
Starbur, Bristly	*Acanthospermum hispidum*
Sunflower, Common	*Helianthus annuus*
Trumpetcreeper	*Campsis redicans*
Velvetleaf	*Abutilon theophrasti*
Venice Mallow	*Hibiscus trionum*
Waterhemp, Common	*Amaranthus rudis*
Waterhemp, Tall	*Amaranthus tuberculatos*
Witchweed	*Striga asiatica*
Yellow Rocket	*Barbarea vulgaris*

STORAGE AND DISPOSAL

Do not contaminate water, food or feed by storage or disposal.

Prohibitions

Open dumping is prohibited. Do not reuse empty container.

Pesticide Storage

Store above 32°F in original containers only. If product freezes, return to room temperature and agitate to reconstitute. Keep container closed when not in use. Do not store near food or feed. In case of spill or leak on floor or paved surfaces, soak up with sand, earth or synthetic absorbent. Remove to chemical waste area.

Pesticide Disposal

Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture or rinsate is a violation of federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency or the Hazardous Waste Representative at the nearest EPA Regional Office for guidance.

CONTAINER DISPOSAL

Metal Containers: Triple rinse (or equivalent); then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill or by other procedures approved by state and local authorities.

Plastic Containers: Triple rinse (or equivalent); then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, by incineration or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

Bulk and Mini-Bulk Containers

Container Disposal: When the container is empty, replace the cap and seal all openings that have been opened during use; and return the container to the point of purchase, or to a designated location named at the time of purchase of the product. This container must only be refilled with this pesticide product. **DO NOT REUSE THE CONTAINER FOR ANY OTHER PURPOSE.** Prior to refilling, inspect carefully for damage such as cracks, punctures, abrasions, worn-out threads and closure devices. Check for leaks after refilling and before transporting. Do not transport if this container is damaged or leaking. If the container is damaged, leaking or obsolete, contact Syngenta at 1-800-888-8372. If not returned to the point of purchase or to a designated location, triple rinse emptied container and offer for recycling. Disposal of this container must be in compliance with state and local regulations.

Container Precautions: Before refilling, inspect thoroughly for damage, such as cracks, punctures, bulges, dents, abrasions and damaged or worn threads on closure devices.

REFILL ONLY WITH REFLEX. The contents of this container cannot be completely removed by cleaning. Refilling with materials other than Reflex will result in contamination and may weaken container.

After filling and before transporting, check for leaks.

Do not refill or transport damaged or leaking container.

CONTAINER IS NOT SAFE FOR FOOD, FEED OR DRINKING WATER.

For non-emergency (e.g., current product information) call
Syngenta Crop Protection at 1-800-334-9481

Manufactured for:
Syngenta Crop Protection, Inc.
Greensboro, North Carolina 27409
www.syngenta-us.com

SCP 993A-L1C 0207

Reflex®

Herbicide

For Control of Weeds in Cotton, Dry Beans, Snap Beans and Soybeans

Active Ingredient:

Sodium salt of fomesafen 5-[2-chloro-4-(trifluoromethyl) phenoxy]-N-(methylsulfonyl)-2-nitrobenzamide	22.8%*
Other Ingredients:	77.2%
Total:	100.0%

*Equivalent to 21.7% fomesafen or 2 pounds fomesafen active ingredient per gallon.

See additional precautionary statements and directions for use inside booklet.

AGRICULTURAL USE REQUIREMENTS
Use this product only in accordance with its labeling and with the Worker Protection Standard, 40 CFR part 170. Refer to supplemental labeling under "Agricultural Use Requirements" in the Directions for Use section for information about this standard.

EPA Reg. No. 100-993 EPA Est. No. 100-NE-001

FIRST AID

If in eyes: Hold eye open and rinse slowly and gently with water for 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing. Call a Poison Control Center or doctor for treatment advice.

If swallowed: Call a Poison Control Center or doctor immediately for treatment advice. Have person sip a glass of water if able to swallow. Do not induce vomiting unless told to by a Poison Control Center or doctor. Do not give anything by mouth to an unconscious person.

If on skin or clothing: Take off contaminated clothing. Rinse skin immediately with plenty of water for 15-20 minutes. Call a Poison Control Center or doctor for treatment advice.

If inhaled: Move person to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably mouth-to-mouth, if possible. Call a Poison Control Center or doctor for further treatment advice.

NOTE TO PHYSICIAN: Probable mucosal damage may contraindicate the use of gastric lavage.

Have the product container or label with you when calling a poison control center or doctor or going for treatment.

HOTLINE NUMBER: For 24 Hour Medical Emergency Assistance (Human or Animal) Or Chemical Emergency Assistance (Spill, Leak, Fire or Accident) Call 1-800-888-8372.

2.5 gallons

Net Contents

KEEP OUT OF REACH OF CHILDREN.

DANGER-PELIGRO

Si usted no entiende la etiqueta, busque a alguien para que se la explique a usted en detalle. (If you do not understand the label, find someone to explain it to you in detail.)

Precautionary Statements

Hazards to Humans and Domestic Animals

CORROSIVE. CAUSES IRREVERSIBLE EYE DAMAGE. DUE TO CORROSIVE NATURE, MAY BE HARMFUL OR FATAL IF SWALLOWED. HARMFUL IF INHALED OR ABSORBED THROUGH SKIN. Do not get in eyes, on skin or on clothing. Avoid breathing vapors or spray mist.

Personal Protective Equipment (PPE)

Applicators and other handlers must wear:

- Long-sleeved shirt and long pants
- Chemical-resistant gloves such as barrier laminate or viton
- Shoes plus socks
- Protective eyewear

Discard clothing and other absorbent materials that have been drenched or heavily contaminated with this product's concentrate. Do not reuse them. Follow manufacturer's instructions for cleaning/maintaining PPE. If no such instructions for washables, use detergent and hot water. Keep and wash PPE separately from other laundry.

When handlers use closed systems, enclosed cabs, or aircraft in a manner that meets the requirements listed in the Worker Protection Standard (WPS) for agricultural pesticides [40 CFR 170.240(d)(4-6)], the handler PPE requirements may be reduced or modified as specified in the WPS.

User Safety Recommendations

Users should:

- Wash hands before eating, drinking, chewing gum, using tobacco or using the toilet.
- Remove clothing immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing.
- Remove PPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change into clean clothing.

Environmental Hazards

Do not apply directly to water, or to areas where surface water is present, or to intertidal areas below the mean high water mark. Do not contaminate water when disposing of equipment washwaters. Do not apply when weather conditions favor drift from target area.

This chemical is known to leach through soil into groundwater under certain conditions as a result of label use. Use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in groundwater contamination.

Storage and Disposal

Do not contaminate water, food or feed by storage or disposal.

Prohibitions

Open dumping is prohibited. Do not reuse empty container.

Pesticide Storage

Store above 32°F in original containers only. If product freezes, return to room temperature and agitate to reconstitute. Keep container closed when not in use. Do not store near food or feed. In case of spill or leak on floor or paved surfaces, soak up with sand, earth or synthetic absorbent. Remove to chemical waste area.

Pesticide Disposal

Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture or rinsate is a violation of federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency or the Hazardous Waste Representative at the nearest EPA Regional Office for guidance.

Container Disposal

Triple rinse (or equivalent); then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, by incineration or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

Product of China
Formulated in the USA

Manufactured for:
Syngenta Crop Protection, Inc.
Greensboro, North Carolina 27409
www.syngenta-us.com

SCP 993A-L1C 0207

syngenta®